

DOE/ER-0144/9
(DE91011221)



Summaries of FY 1991 Research in the Chemical Sciences

AUGUST 1991

U.S. Department of Energy
Office of Energy Research
Division of Chemical Sciences

Prepared by
Office of Scientific and
Technical Information

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

DOE/ER-0144/9

(DE91011221)

August 1991

Distribution Categories UC-400 and UC-401



Summaries of FY 1991 Research in the Chemical Sciences

U.S. Department of Energy
Office of Energy Research
Division of Chemical Sciences

This report was compiled for the Office of Energy Research from project summaries contained in the Research-In-Progress (RIP) database of the Office of Scientific and Technical Information, Oak Ridge, Tennessee. The RIP database describes new and ongoing energy and energy-related research projects carried out or sponsored by the Department of Energy.

Contents

PREFACE	vii	University of Arizona	34
CHEMICAL SCIENCES DIVISION	viii	Boston University	34
PROGRAM SUMMARIES	ix	Brandeis University	34
LABORATORY ADMINISTRATION	xi	California Institute of Technology	35
		University of California, Berkeley	35
		University of California, Irvine	35
		University of California, Los Angeles	36
		University of California, Santa Barbara	36
		Clemson University	36
		University of Colorado	37
		Columbia University	37
		Dartmouth College	38
		University of Houston	38
		Marquette University	38
		Massachusetts Institute of Technology	39
		University of Massachusetts at Boston	39
		University of Minnesota	39
		National Institute of Standards and Technology, Gaithersburg	39
		University of North Carolina at Chapel Hill	40
		University of North Carolina at Charlotte	40
		Northwestern University	40
		Ohio State University	41
		Oregon Graduate Institute of Science and Technology	41
		Pennsylvania State University, University Park	41
		University of Pittsburgh	42
		Portland State University	42
		Princeton University	42
		University of Rochester	43
		Rutgers University	44
		University of South Florida	44
		Stanford University	44
		Syracuse University	45
		University of Tennessee	45
		University of Texas at Austin	45
		Washington State University	46
		Wayne State University	46
		Chemical Physics	
		Aerospace Corporation	47
		University of Akron	47
		Arizona State University	47
		University of Arizona	47
		University of California, Los Angeles	48
		Catholic University of America	48
		University of Chicago	48
		University of Colorado	49
		Columbia University	49
		Cornell University	50
		Emory University	50
		Georgia Institute of Technology	51
		University of Georgia	51
		Harvard University	51
		University of Illinois at Chicago	52
		Johns Hopkins University	52
		University of Kentucky	53
		Massachusetts Institute of Technology	53
		University of Massachusetts at Amherst	54
NATIONAL LABORATORIES			
Photochemical and Radiation Sciences			
Ames Laboratory	1		
Argonne National Laboratory	2		
Brookhaven National Laboratory	3		
Lawrence Berkeley Laboratory	4		
Notre Dame Radiation Laboratory	5		
Solar Energy Research Institute	7		
Chemical Physics			
Ames Laboratory	8		
Argonne National Laboratory	8		
Brookhaven National Laboratory	9		
Lawrence Berkeley Laboratory	10		
Lawrence Livermore National Laboratory	11		
Pacific Northwest Laboratory	12		
Sandia National Laboratories, Livermore	12		
Atomic Physics			
Argonne National Laboratory	14		
Brookhaven National Laboratory	14		
Lawrence Berkeley Laboratory	15		
Oak Ridge National Laboratory	15		
Sandia National Laboratories, Albuquerque	16		
Chemical Energy			
Ames Laboratory	16		
Argonne National Laboratory	18		
Brookhaven National Laboratory	19		
Lawrence Berkeley Laboratory	19		
Los Alamos National Laboratory	21		
Oak Ridge National Laboratory	21		
Pacific Northwest Laboratory	23		
Solar Energy Research Institute	23		
Separations and Analysis			
Ames Laboratory	23		
Argonne National Laboratory	24		
Brookhaven National Laboratory	25		
Idaho National Engineering Laboratory	25		
Lawrence Berkeley Laboratory	25		
Oak Ridge National Laboratory	26		
Pacific Northwest Laboratory	28		
Heavy Element Chemistry			
Argonne National Laboratory	29		
Lawrence Berkeley Laboratory	29		
Los Alamos National Laboratory	30		
Oak Ridge National Laboratory	30		
Chemical Engineering Sciences			
Lawrence Berkeley Laboratory	31		
Los Alamos National Laboratory	31		
Sandia National Laboratories, Livermore	32		
OFFSITE INSTITUTIONS			
Photochemical and Radiation Sciences			
University of Akron	33		
University of Alabama	33		
Arizona State University	33		

CONTENTS

University of Michigan	54	University of Minnesota	77
University of Minnesota	54	University of Missouri at Columbia	77
National Institute of Standards and Technology, Gaithersburg	55	University of Nevada	77
University of New Orleans	56	University of New Mexico	78
University of North Carolina at Chapel Hill	56	University of North Carolina at Chapel Hill	78
University of Pennsylvania	56	Northwestern University	78
University of Pittsburgh	57	University of Oklahoma	79
Princeton University	57	University of Oregon	79
Rensselaer Polytechnic Institute	58	Pennsylvania State University, University Park	80
Rice University	58	University of Pennsylvania	81
University of Rochester	59	University of Pittsburgh	82
SRI International	59	Purdue University	82
University of Southern California	59	Rensselaer Polytechnic Institute	83
Stanford University	60	University of Rochester	83
State University of New York at Buffalo	60	Rutgers University	83
State University of New York at Stony Brook	61	University of South Carolina	84
University of Wisconsin at Madison	61	University of Southern California	84
Atomic Physics		Southern Illinois University	84
California State University, Fullerton	61	Stanford University	85
Clark Atlanta University	62	State University of New York at Binghamton	85
University of Colorado	62	State University of New York at Buffalo	86
Cornell University	62	Texas A & M University	86
Georgia Institute of Technology	63	University of Texas at Austin	87
Harvard University	63	Tulane University	87
Kansas State University	63	University of Utah	87
University of Louisville	64	Virginia Polytechnic Institute and State University	88
National Institute of Standards and Technology, Gaithersburg	64	University of Washington	88
University of Nebraska	64	Wayne State University	89
University of Nevada	65	University of Wisconsin at Madison	89
University of New Mexico	65	University of Wisconsin at Milwaukee	90
University of Oregon	65	Yale University	90
Pennsylvania State University, Lehman	65	Separations and Analysis	
University of Pittsburgh	66	Auburn University	91
Rice University	66	Brigham Young University	91
University of Rochester	66	Brown University	92
University of Tennessee	66	University of California, Los Angeles	92
Texas A & M University	67	Columbia University	92
University of Texas at Austin	67	University of Delaware	92
University of Toledo	67	Duke University	93
Vanderbilt University	68	University of Florida	93
University of Virginia	68	The George Washington University	93
Western Michigan University	68	Georgia Institute of Technology	94
The College of William and Mary	68	Hampton University	94
Chemical Energy		University of Houston	94
Auburn University	69	University of Idaho	95
California Institute of Technology	69	University of Illinois at Urbana-Champaign	95
University of California, Irvine	69	Kansas State University	95
University of California, Santa Barbara	70	Lehigh University	96
Colorado State University	70	Michigan State University	96
University of Colorado	71	University of Michigan	96
University of Connecticut	71	University of Minnesota	96
University of Delaware	71	University of Missouri at Rolla	97
Harvard University	72	National Institute of Standards and Technology, Gaithersburg	97
University of Illinois at Urbana-Champaign	72	University of North Carolina at Chapel Hill	97
Indiana University	73	University of Oklahoma	98
University of Iowa	74	Purdue University	98
University of Kentucky	74	Rensselaer Polytechnic Institute	98
Lehigh University	74	State University of New York at Buffalo	99
Louisiana State University	75	Syracuse University	99
University of Louisville	75	University of Tennessee	99
Massachusetts Institute of Technology	75	Texas A & M University	100
University of Massachusetts at Amherst	76		
University of Michigan	76		

Texas Tech University	101	North Carolina State University	108
University of Texas at Austin	101	University of Pennsylvania	108
University of Utah	101	Princeton University	109
Virginia Commonwealth University	102	Purdue University	109
University of Wyoming	102	Stanford University	109
Heavy Element Chemistry		State University of New York at Stony Brook	109
Florida State University	103	University of Virginia	110
University of New Mexico	103	University of Wisconsin at Madison	110
Ohio State University	103	Yale University	110
SRI International	103		
University of Tennessee	104	Small Business Innovation Research	
Chemical Engineering Sciences		Chromex, Inc.	111
University of California, San Diego	104	Membrane Technology & Research, Inc.	111
Clarkson University	104	Southwest Sciences, Inc.	111
Colorado State University	105		
Cornell University	105	ADDENDUM	113
University of Delaware	106	SPECIAL FACILITIES	115
University of Illinois at Chicago	106	FY1991 EQUIPMENT FUNDS	129
Johns Hopkins University	106	SELECTED TOPICS	131
University of Maryland	107	INSTITUTION INDEX	133
University of Massachusetts at Amherst	107	INVESTIGATOR INDEX	135
National Institute for Petroleum and Energy Research	107		
National Institute of Standards and Technology, Boulder	108		

PREFACE

This summary book is published annually to provide information on research supported by the Department of Energy's Division of Chemical Sciences, which is one of five Divisions of the Office of Basic Energy Sciences in the Office of Energy Research.

These summaries provide the scientific and technical public, as well as the legislative and executive branches of the Government, information, either generally or in some depth, about the Chemical Sciences program. Areas of research supported are indicated in the section headings, the "Selected Topics of General Interest" list, and the summaries themselves. Energy technologies that may be advanced by use of the basic knowledge generated in this program are included in the "Selected Topics of General Interest" list and are often referenced in the summaries.

Scientists interested in proposing research for support will find the publication useful for gauging the scope of the present basic research program and its relationship to their interests. Proposals that expand this scope may also be considered or directed to more appropriate offices. The primary goal of the research summarized here is to add significantly to the knowledge base on which existing and future efficient and safe energy technologies can evolve. As a result, scientific excellence is a major criterion applied in the selection of research supported by the Division of Chemical Sciences, but another important consideration is emphasis on science that

is advancing in ways that will produce new information related to energy.

The program takes place in several different kinds of performing organizations. About one-third of the projects are at DOE laboratories and the rest mostly at universities, with a small number of projects at industrial laboratories. In DOE laboratories, much of the research utilizes special unique facilities which, in some instances, are national user facilities. These are described in a separate section of this publication.

Another section of this publication includes summaries of projects funded during FY 1991 by the Small Business Innovation Research (SBIR) Program Office in response to technical topics submitted by the Division of Chemical Sciences to the annual SBIR Solicitation.

Questions about the details of an individual project may be directed to the investigators involved or the persons in charge at DOE laboratories (who are identified at appropriate places in this publication). Other questions about the program may be directed to the undersigned.

Robert S. Marianelli, Director
Division of Chemical Sciences
Office of Basic Energy Sciences

**Chemical Sciences Division
Office of Energy Research
U.S. Department of Energy
Washington, DC 20585**

Please Note: All 353 phone prefixes have been changed to 903

OFFICE OF THE DIVISION DIRECTOR

Division Director	Dr. Robert S. Marianelli	(301) 353-5804
Special Assistant	Dr. George A. Fisk*	(301) 353-5804
Secretary	Mrs. Peggy Winpigler	(301) 353-5804

Fundamental Interactions Branch

Branch Chief	Dr. Allan H. Laufer	(301) 353-5820
Secretary	Miss Melissa Cockerham	(301) 353-5820
Photochemical and Radiation Sciences		
Technical Manager	Dr. Mary E. Gress	(301) 353-5820
Chemical Physics		
Technical Manager	Dr. William H. Kirchhoff	(301) 353-5820
Atomic Physics		
Technical Manager	Dr. J. V. Martinez	(301) 353-5820

Processes and Techniques Branch

Branch Chief	Dr. F. Dee Stevenson	(301) 353-5802
Secretary	Mrs. Lori Wiles	(301) 353-5802
Chemical Energy		
Technical Manager	Dr. Stephen A. Butter	(301) 353-5802
Technical Manager	Dr. William S. Millman†	(301) 353-5802
Technical Manager	Dr. John L. Burnett	(301) 353-5804
Separations and Analysis		
Technical Manager	Dr. John L. Burnett	(301) 353-5802
Technical Manager	Dr. Richard L. Gordon‡	(301) 353-5802
Chemical Engineering Science		
Technical Manager	Dr. F. Dee Stevenson	(301) 353-5802
Heavy Element Chemistry		
Technical Manager	Dr. John L. Burnett	(301) 353-5804

*On leave from Combustion Research Facility, Sandia National Laboratories, Livermore.

†On leave from University of Wisconsin, Milwaukee.

‡On leave from Pacific Northwest Laboratory.

PROGRAM SUMMARIES

Each Branch of the Division of Chemical Sciences is divided into programs that cover various disciplines. The following summaries describe these programs. The staff members responsible for each program are indicated on page viii.

Fundamental Interactions Branch (KC-03-01)

Photochemical and Radiation Sciences (KC-03-01-01)

The Photochemical and Radiation Sciences program consists of research on the interactions of radiation with matter. Emphasis is placed on fundamental research in solar photochemical energy conversion, whereby fuels or energy may be produced by visible light excitation of small molecules or solids. The photochemistry research includes organic and inorganic photocatalysis in homogeneous and heterogeneous media, electron transfer rates and mechanisms, photosynthesis, and photoelectrochemistry. The radiation chemistry research is concerned with the chemical effects produced by absorption of energy from ionizing radiation. A small part of the program is devoted to research in hot atom chemistry, i.e., the study of the effects of nuclear decay and the consequent release of energy on chemical reactions.

Chemical Physics (KC-03-01-02)

The Chemical Physics program supports research in a diverse set of disciplines with a goal of providing basic knowledge in areas related to the nation's energy needs. A significant portion of the program is in the many-faceted area of chemical kinetics, including energy transfer, chemical dynamics involving state-selected chemistry, unimolecular and bimolecular reaction kinetics, as well as the reactions of clusters. Research efforts in molecular structure, spectroscopy, and theoretical chemistry are also well represented in this program. In addition, there is a growing effort in surface dynamics.

Special emphasis is placed on basic research related to combustion; spectroscopy, theory, and the kinetics of elementary combustion reactions are of special interest. A major user-oriented facility, the

Combustion Research Facility (CRF) at Sandia Laboratories/Livermore is supported by this program. This laboratory offers the use of advanced instrumentation to interested combustion scientists from universities, industry, and national laboratories.

Atomic Physics (KC-03-01-03)

The Atomic Physics program supports experimental and theoretical efforts associated with the study of atom and atomic ion structures, energy levels and lifetimes of quantum states, and of transport and exchange processes characterizing transfer of energy and momentum. These studies strive to obtain the most accurate and complete fundamental knowledge of the properties and interactions of photons, electrons, atoms, and ions. Continued emphasis of this research is on the understanding of relatively high energy atomic physics that involves atoms stripped of all or almost all electrons and of atoms and ions in which electrons are promoted to upper energy levels. The study of processes that lead to the production of coherent radiation and of how its statistical properties are manifest in atomic physics also constitutes part of this program.

Facility Operations (KC-03-01-04)

DOE operates large scientific facilities for the benefit of the scientific community. Major user facilities permit forefront research to be conducted in areas important to DOE by scientists from industry and universities in addition to DOE contractors/grantees. Operating support for these expensive, unique facilities that are open to all qualified researchers is provided by DOE. Many of the facilities are user oriented. The four operated by Chemical Sciences are: the Combustion Research Facility (CRF) at Sandia/Livermore, the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory, the Stanford Synchrotron Radiation Laboratory (SSRL) at Stanford, and, shared with the Materials Sciences Division, the National Synchrotron Light Source (NSLS) at Brookhaven. They represent research resources for the general scientific community, and qualified scientists not associated with the host laboratory are encouraged to make use of them. However, any activity that can be carried out

at commercially available laboratories is not appropriate for these DOE-supported facilities. The process by which an off-site scientist can use a facility is discussed in each summary.

In addition, another facility at Oak Ridge is operated as a service to the scientific community: the Radiochemical Engineering Development Center (REDC).

Other facilities described in the "Special Facilities" section are also available for use through collaboration with staff scientists. The names of individuals to contact for further information and technical data on available instrumentation at each facility are described.

Processes and Techniques Branch (KC-03-02)

Chemical Energy (KC-03-02-01)

This program includes basic chemistry research related to chemical transformations or conversions which are fundamental to new or existing concepts of energy production and storage. Of particular interest are those research activities with the objectives of understanding the chemical aspects of (1) catalysis, both heterogeneous and homogeneous; (2) the chemistry of fossil resources, particularly coal, including characterization and transformation; (3) the conversion of biomass and related cellulosic wastes; and (4) the chemistry of precursors to advanced materials. The disciplines of organic, organometallic, inorganic, physical, thermo-, and electrochemistry are central to these programs. The emphasis is on understanding the fundamental chemical principles underlying the new and developing technologies and on innovative chemical research with potential for new energy concepts.

Separations and Analysis (KC-03-02-02)

The separations part of the program supports basic research directed toward improving our understanding of methods for separating mixtures of gases, liquids, solids, and their component molecules, cations, and anions. The program covers a broad spectrum of separations concepts, including membrane processes, extraction at both standard and supercritical conditions, adsorption, chromatography, photodissociation, complexation, etc. The research involves elucidating fundamental chemical phenomena for improved or new separations rather than developing specific processes.

The analysis part of the program supports research on phenomena basic to analytical methods, the goal being to improve sensitivity, reliability, and/or productivity of analytical determinations. Chemical and physical principles which can lead to entirely new methods of analysis are investigated, although this program does not support instrument development. Research progress is reported quickly in the open literature so that those interested in instrument development can build on work supported herein. The program is aimed at obtaining a thorough understanding of the basic chemistry of analytical techniques so that their utility can be improved, rather than solving specific problems in analysis.

Heavy Element Chemistry (KC-03-02-03)

The Heavy Element Chemistry program focuses on a study of the chemical and certain physical properties of the actinide elements, principally the transuranium elements, because of the importance of these elements to DOE's nuclear technology programs and to an understanding of the basic science in general. A variety of investigations are pursued, including (1) organometallic chemistry, (2) the chemistry of excited spectroscopic states, (3) thermochemistry of actinide elements and compounds, (4) the chemistry of actinides in near-neutral aqueous solutions and the reactions of aqueous actinide ions with various complexing agents, (5) the development of preparative methods for actinide metals and compounds, and (6) characterization of actinides under pressure. This research is performed principally at the national laboratories because of facilities required for handling radioactivity.

Chemical Engineering Sciences (KC-03-02-04)

This program addresses energy-related aspects of chemically related engineering topics, including thermodynamics, turbulence related to combustion, and physical and chemical rate processes. Particular attention is given to experimental and theoretical aspects of phase equilibria, especially of mixtures, including supercritical phenomena, and to the physics of gas phase turbulence. Also included are fundamental studies of thermophysical and thermochemical properties. Emphasis is given to improving and/or developing the scientific base for engineering generalizations and their unifying theories.

LABORATORY ADMINISTRATION

Listed below, by laboratory and department or division, are persons who are in charge of the Division of Chemical Sciences projects at DOE laboratories. These individuals are laboratory, department, or division administrators who can provide information about specific programs or refer inquiries to appropriate individuals.

AMES LABORATORY

Iowa State University
Ames, IA 50011

Chemical Sciences—Fundamental Interactions

A. DePristo
Phone: Commercial (515) 294-9924

Chemical Sciences—Processes and Techniques

J. H. Espenson
Phone: Commercial (515) 294-5730

ARGONNE NATIONAL LABORATORY

9700 South Cass Avenue
Argonne, IL 60439

Chemical Technology Division

M. J. Steindler
Phone: Commercial (708) 972-4314 or
FTS 972-4314

Chemistry Division

L. M. Stock
Phone: Commercial (708) 972-3570 or
FTS 972-3570

Physics Division

H. G. Berry
Phone: Commercial (708) 972-4039 or
FTS 972-4039

BROOKHAVEN NATIONAL LABORATORY

Upton, Long Island, NY 11973

Applied Science Department

L. Petrakis
Phone: Commercial (516) 282-3037 or
FTS 666-3037

Chemistry Department

N. Sutin
Phone: Commercial (516) 282-4301 or
FTS 666-4301

National Synchrotron Light Source

D. McWhan
Phone: Commercial (516) 282-4966 or
FTS 666-4966

IDAHO NATIONAL ENGINEERING LABORATORY

EG&G Idaho, Inc., P. O. Box 1625
Idaho Falls, ID 83415

Chemical Sciences Group

C. A. Allen
Phone: Commercial (208) 526-0250 or
FTS 583-0250

LAWRENCE BERKELEY LABORATORY

University of California
Berkeley, CA 94720

Applied Sciences Division

E. J. Cairns
Phone: Commercial (415) 486-5028 or
FTS 451-5028

Chemical Biodynamics Division

S.-H. Kim
Phone: Commercial (415) 486-4355 or
FTS 451-4355

Chemical Sciences Division

N. Phillips
Phone: Commercial (415) 486-6382 or
FTS 451-6382

Nuclear Science Division

T. J. M. Symons
Phone: Commercial (415) 486-5670 or
FTS 451-5670

**LAWRENCE LIVERMORE NATIONAL
LABORATORY**

University of California
P.O. Box 808
Livermore, CA 94550

R. N. Schock
Phone: Commercial (415) 422-6189 or
FTS 532-6189

LOS ALAMOS NATIONAL LABORATORY

University of California
P.O. Box 1663
Los Alamos, NM 87545

A. Hartford
Phone: Commercial (505) 667-8680 or
FTS 843-8680

NOTRE DAME RADIATION LABORATORY

University of Notre Dame
Notre Dame, IN 46556

R. H. Schuler
Phone: Commercial (219) 239-7502

OAK RIDGE NATIONAL LABORATORY

P.O. Box 2008
Oak Ridge, TN 37831

Analytical Chemistry Division

W. D. Shults
Phone: Commercial (615) 574-4881 or
FTS 624-4881

Chemical Technology Division

R. K. Genung
Phone: Commercial (615) 574-6275 or
FTS 624-6275

Chemistry Division

M. L. Poutsma
Phone: Commercial (615) 574-5028 or
FTS 624-5028

Physics Division

S. Datz
Phone: Commercial (615) 574-4984 or
FTS 624-4984

PACIFIC NORTHWEST LABORATORY

P.O. Box 999
Richland, WA 99352

Chemical Sciences Department

B. R. Stults
Phone: Commercial (509) 375-2687

Molecular Sciences Research Center

M. Knotek
Phone: Commercial (509) 375-2272

**SANDIA NATIONAL LABORATORIES,
ALBUQUERQUE**

P.O. Box 5800
Albuquerque, NM 87185

F. L. Vook
Phone: Commercial (505) 844-9304 or
FTS 844-9304

**SANDIA NATIONAL LABORATORIES,
LIVERMORE**

Livermore, CA 94551

Combustion Research Facility

J. S. Binkley
Phone: Commercial (415) 294-2174 or
FTS 234-2174

SOLAR ENERGY RESEARCH INSTITUTE

1617 Cole Boulevard
Golden, CO 80401

**Fuels and Chemicals Research and
Engineering Division**

A. J. Nozik
Phone: Commercial (303) 231-1953 or
FTS 327-1953

S. R. Bull
Phone: Commercial (303) 231-1200 or
FTS 327-1200

NATIONAL LABORATORIES

Photochemical and Radiation Sciences

Ames Laboratory
Iowa State University
Ames, IA 50011

Fundamental Interactions Program **\$600,000**

1. Electrochemical and Optical Studies of Model Photosynthetic Systems

Cotton, T.M.
Comm. 515-294-9887

The objective of this research is the preparation of model systems that have the photoinduced electron-transfer characteristics of the photosynthetic reaction center. A wide spectrum of systems is being investigated, ranging from model systems based completely on synthetic molecules or analogs of natural molecules, to systems in which most, or all, of the elements have been derived from natural sources. Excluded are those constructions that are solely reconstitutions of functional *in vivo* parts produced by biochemical separations. The fundamental mode of attack is the use of monolayers and multilayers to produce the systems of interest. Three approaches are being followed: preparation of spread monolayers at the air/water interface, self-assembly adsorption techniques, and formation of multilayer systems by the Langmuir-Blodgett film transfer method. The principal instrumental techniques used for characterization include electrochemistry, laser Raman spectroscopy, and scanning tunneling microscopy. Additional information is obtained by optical absorption and linear dichroic spectroscopy of the monolayer systems. [2.0 FTE]

2. Photoinduced Electron-Transfer Reactions in Protein Matrices

Kostic, N.M.
Comm. 515-294-7715

This research focuses on two rate-determining factors in photoinduced electron-transfer reactions: the pathway for the transfer from the electron donor to the acceptor, and the thermodynamic driving force. The donors are ferrocyanochrome *c* (in the ground electronic state) and zinc cytochrome *c* (in the triplet excited state), while the acceptor is cuprisplastocyanin. These proteins are studied because the redox-active metal ions in them are fully characterized, fixed in three dimensions, and replaceable with various nonbiological metals. The proteins are associated flexibly by electrostatic forces, and both rigidly and flexibly by covalent crosslinks. The rates of electron transfer within the complexes have been determined by laser flash kinetic spectroscopy. The experiments are designed to show whether ground-state electron-transfer reactions require rearrangement of the donor and the acceptor into

an optimal configuration. Comparisons of kinetics of the excited-state reactions in precursor and encounter donor-acceptor complexes with those of the corresponding ground-state reactions have elucidated the role of transfer pathway and the thermodynamic driving force on the electron-transfer rate. The rate has been shown to depend on the transfer pathway more when the driving force is low than when it is high. Even though the donor and the acceptor are highly charged, their association has been found to depend on hydrophobic as well as electrostatic interactions. [2.0 FTE]

3. Laser Spectroscopy and Electronic Energy Transfer of Light Conversion Systems

Small, G.J.
Comm. 515-294-3859

The primary photoconversion processes of photosynthesis are investigated in order to understand the structure-function relationships that result in the near unit quantum yield and high solar energy conversion efficiency of photosynthetic units. Determination of these relationships is viewed as important to the development of biomimetic solar energy conversion technologies which generate electricity or fuels. The primary photoconversion processes are optical excitation (energy) transfer and electron transport processes in antenna (light harvesting) and reaction center complexes. Laser-based optical frequency domain spectroscopies (e.g., spectral hole burning), developed in this laboratory for biological applications, are used to provide a high resolution window on the primary processes and the electronic structure of the photocatalytic chlorophyll states that drive them. These spectroscopies also yield important information on the interaction between excited chlorophyll states and the protein environment, an interaction that enters into theories of transport dynamics. Photosynthetic units from both purple bacteria and green plants are studied. Data obtained continue to provide fresh insights into energy transfer and electron transport and are used to test existing theoretical models and to develop new models. [2.2 FTE]

4. Ultrafast Spectroscopy and Reaction Dynamics

Struve, W.S.
Comm. 515-294-4276

Ultrafast fluorescence and pump-probe spectroscopies are used to characterize electron excitation transport in naturally occurring and artificial photosynthetic systems. Recent attention has focused on (1) pump-probe studies of energy transfer in linear bacteriochlorophyll (BChl) *c* aggregates from the green bacterium *Chloroflexus auranticus*, (2) polarized time-resolved fluorescence spectroscopy of oriented gels of C-phycocyanin trimers from blue-green algae, and (3) the temperature dependence of single excitation hops in the chlorophyll *a* antenna of photosystem I. The first of these projects is motivated by the fact that these BChl *c* aggregates are spectroscopically identical to BChl *c* oligomers that form spontaneously in solution; this "self-aggregating" property may thus lend

itself to facile construction of artificial antennae. The second project addresses a ubiquitous problem: fluorescence profiles emitted by simple antennae are frequently complicated by the presence of many lifetime components that are difficult to assign to specific energy transfer steps. The use of symmetry and partial orientation of the protein samples in compressed gels promises to yield far more incisive interpretations of such experiments. [2.2 FTE]

Argonne National Laboratory Argonne, IL 60439

Chemistry Division \$5,100,000

5. *Electron Transfer and Energy Conversion*

Miller, J.R.; Meisel, D.
Comm. 708-972-3481; FTS 972-3481

The project explores fundamental questions of electron-transfer reactions and redox catalysis. Special experimental tools enable measurements of how rates of electron transfer between molecules depend on distance, energy, polarity, and angular orientation. These measurements are unusual in their ability to investigate the effect of each of these critical variables without interference from the others and in a quantitative way that enables fundamental examination and development of theory, as exemplified in the recent striking success of theory in predicting temperature dependence. Redox catalysis by small semiconductor particles received fundamental support from knowledge of the electron and surface properties of the particles. Careful measurements of particle sizes, their absorption and emission spectra, and the dynamics of charge transfer in these particles allow insights into present, rudimentary theories, which relate size to bandgap. Stability and reactivity are partially controllable by chemical modification of the particle surface. Chemistry of d- and f-transition elements is investigated with emphasis on electron-transfer reactions and formation of colloids by these elements. [5.9 FTE]

6. *Characterization of Photosynthetic Components*

Norris, J.R.; Bowman, M.K.; Tiede, D.M.
Comm. 708-972-3544; FTS 972-3544

The project objective is to develop systems for use in studies of solar energy conversion. In order to understand and to develop highly efficient forms of artificial solar energy conversion, the basic physical and chemical features of the individual compounds, solvents, matrices, and light-harvesting antennae are required. The focus of these studies is threefold: (1) the transfer of excitation energy prior to charge separation, (2) the properties of isolated molecules relevant to electron transfer, and (3) the interactions responsible for noncovalent binding. Normal and isotopically altered chemicals or special assemblies are provided to enhance the utility of the spectroscopies used in the study of photoinduced charge separation. A unique facility is operated for large-scale culture and isotopic labeling of algae and photosynthetic bacteria. [1.2 FTE]

7. *Photosynthesis Research*

Norris, J.R.; Tang, J.; Thurnauer, M.; Bowman, M.K.; Tiede, D.M.; Wasielewski, M.R.
Comm. 708-972-3544; FTS 972-3544

This project has two main objectives. The first objective is to uncover the basic principles of the chemistry and physics involved in the primary photoinduced charge separation that occurs in photosynthetic bacteria and green organisms. Three areas are emphasized. (1) The mechanism of charge separation as produced by photoinduced electron transfer in natural photosynthesis is probed at the molecular level. (2) Theoretical models for electron transfer are proposed to explain and complement the experimental work. (3) Advanced instrumentation and computer techniques are explored to help establish the mechanisms involved in natural and artificial photosynthesis. The information gained in these studies is used to obtain the second objective, the design and preparation of molecules and molecular assemblages that will convert light energy into useful chemical energy in the laboratory. The systems being studied, mainly by optical and magnetic resonance spectroscopies, include natural, isotopically substituted and chemically manipulated photoactive assemblies, solutions, and compounds. [4.7 FTE]

8. *Reactive Intermediates in Condensed Phases: Radiation and Photochemistry*

Trifunac, A.D.; Jonah, C.D.; Sauer, M.C., Jr.; Bartels, D.M.; Werst, D.W.; Lin, Y.
Comm. 708-972-3483; FTS 972-3483

This project studies short-lived species whose transformations and dynamics define the chemistry of ionization and photoionization. The observed diversity of consequences of ionizing radiation found in chemical and biological systems can be understood by considering fundamental processes involving charge transport, proton transfer, and excited states. The detailed study of short-lived species such as radical cations and electrons provides paradigms for understanding a wide range of fundamental issues of chemical reactivity and is relevant to many technologically important chemical processes. The role of the solvent in modulating the reactivity of such highly reactive species is exemplified by studies of electrons and ions in condensed phase. Molecular segregation is achieved in low-temperature matrices, or "micro-reactors" such as zeolites, allowing detailed studies of condensed phase reactivity of radical cations. This research is conducted using specialized state-of-the-art techniques that include a picosecond linac, femtosecond laser and time-domain magnetic resonance, and optical detection methods. [8.2 FTE]

9. *Artificial Photosynthesis*

Wasielewski, M.R.
Comm. 708-972-3538; FTS 972-3538

The purpose of artificial photosynthesis research is to design and prepare molecules that will convert light energy into useful chemical energy in the laboratory. The primary photochemistry of natural photosynthesis serves as a model for highly-efficient conversion of light energy into chemical energy. Natural photosynthetic charge separation may be improved by producing a more rugged molecular system that can function as a good photocatalyst in harsher chemical environments than those

encountered with proteins. The initial events of photosynthesis consist of a sequence of picosecond electron transfer reactions between donor and acceptors that are positioned at critical distances and orientations relative to one another within a large protein. Thus, donor-acceptor molecules that maintain well-defined structural relationships between the various donors and acceptors are synthesized and studied. Molecules containing two or more covalently linked electron donors and acceptors are being developed to efficiently convert light energy into stored chemical energy. The photophysics and photochemistry of these molecules are examined with primary emphasis on ultrafast light-induced electron-transfer reactions and high-yield energy storage. [3.9 FTE]

Brookhaven National Laboratory Upton, Long Island, NY 11973

Department of Applied Science \$1,000,000

10. Porphyrin Chemistry

Fajer, J.; Barkigia, K.M.; Renner, M.W.;
Thompson, M.A.
Comm. 516-282-4521; FTS 666-4521

Porphyrin derivatives mediate a wide spectrum of bioenergetic reactions ranging from light-harvesting and energy conversion in photosynthesis to multielectron transfers in reactions as diverse as nitrogen assimilation, regiospecific syntheses, and conversion of carbon dioxide to methane. This project seeks to define the electronic configurations that control these multifaceted mechanisms by a combination of experimental, structural, and theoretical approaches that considers the cumulative effects of macrocycle, substituents, metal, ligands, conformations, aggregation, and environment (protein or solvent) in fine-tuning the photophysics, photochemistry, and electron-transfer properties of porphyrins. The work encompasses photochemistry, spectroelectrochemistry, magnetic resonance (ESR, ENDOR, NMR), X-ray diffraction, and synchrotron radiation techniques that are closely supported by several theoretical methods (extended Hückel, INDO, and molecular dynamics). The goals of the work are to identify and characterize the transients and mechanisms in these photosynthetic and biocatalytic reactions, and to provide specific guidelines for the development of synthetic photocatalytic systems. [5.8 FTE]

11. Electrochemistry and Photoelectrochemistry

Feldberg, S.W.; Smalley, J.F.
Comm. 516-282-4480; FTS 666-4480

The project comprises experimental and theoretical studies of electrochemical and photoelectrochemical phenomena. The major experimental effort focuses on studies of fast interfacial rate processes associated with electron transfer, ion transfer, and surface reconstruction or reorganization. A laser-induced-temperature-jump technique developed in an earlier phase of this work is one of the tools being used to characterize processes that can occur in the microsecond and submicrosecond time domain. Results in this previously inaccessible time domain will help to elucidate the mechanisms of these heterogeneous phenomena. Computer simulation of electrochemical and

photoelectrochemical problems is a continuing contribution of this project. A new approach to computer simulation has been developed that greatly enhances the power of the commonly used explicit-finite-difference methodology without compromising its simplicity and flexibility. Some applications include simulations of the cyclic voltametric behavior of a variety of electrochemical mechanisms, of diffusion-migration effects at ultramicroelectrodes, and of photoresponses of semiconductor electrodes. [2.5 FTE]

Chemistry Department \$3,010,000

12. Thermal and Photoinduced Reactions in Solution

Creutz, C.; Newton, M.; Seltzer, S.; Sutin, N.;
Brunschwig, B.S.; Fujita, E.;
Comm. 516-282-4359; FTS 666-4359

This program addresses three areas fundamental to the efficient capture and storage of light energy: (1) excited-state formation, chemistry, and photophysics; (2) energy transduction by electron-transfer reactions; and (3) energy storage through chemical transformations. Theoretical and experimental efforts are elucidating the factors controlling electron-transfer rates and excited-state lifetimes; the roles of electronic configuration, separation distance, nuclear configuration and free-energy changes, and solvent dynamics are being investigated through studies of transition-metal complexes. The long-term storage of solar energy as fuels or valuable chemicals requires efficient coupling of light-absorption and chemical transformation processes. Mechanistic studies of the photoinduced and thermal olefin *cis-trans* isomerization address the nature of this coupling in the purple membrane proton pump, a solar energy converter which operates through photocatalyzed and protein-catalyzed *cis-trans* isomerization of its bound retinal. Chemical and mechanistic studies of transition-metal centers in high and low oxidation states are being conducted because such centers can couple photoinduced electron-transfer processes to the bond-forming reactions required in the photodecomposition of water or the photoreduction of carbon dioxide to useful chemicals. [13.6 FTE]

13. Radiation Chemistry

Schwarz, H.A.; Bielski, B.H.J.; Holroyd, R.A.;
Cabelli, D.E.; Wishart, J.F.
Comm. 516-282-4330; FTS 666-4330

This program uses pulse radiolysis and photolysis to study the behavior of transient chemical species. Principal areas of investigation are: (1) properties and reactions of electrons in dielectric fluids; (2) photoionization in dielectric fluids; (3) formation and reactions of transition-metal complexes in unusual oxidation states; (4) intramolecular electron-transfer rates; and (5) the nature, thermodynamics, and reactions of radicals produced in aqueous solutions. The studies of electrons in dielectric fluids are of prime importance in understanding the basic processes of radiation chemistry, in the development of new detectors for high-energy physics, and in controlling dielectric breakdown in transformers. The studies of transition-metal complexes are important in developing and understanding certain homogeneous catalysis systems and methods of chemical storage of solar energy. [7.7 FTE]

14. *Hot Atom Chemistry*

Wolf, A.P.; Ferrieri, R.A.

Comm. 516-282-4397; FTS 666-4397

The intent of this program is to investigate the unusual chemical reactions that can be promoted through the interaction of translationally and, in some instances, electronically excited atoms with substrate molecules. The primary concern is how excess kinetic energy affects the fundamental chemistry of these species. A secondary concern is whether hot atoms can be used as a source for generating unusual and sometimes unique reaction intermediates for chemical studies. Studies of this nature can aid in the understanding of the complex chemistry involved, not only in numerous photochemical processes, but in discharge-induced plasmas, and in high-temperature combustion as well. Recently, a new sputtering atom source was developed for generating hot oxygen atoms. The present system enables both transient species and stable end products to be monitored in the gas phase using mass spectrometry. This provides a broad range of information that can be related not only to the primary chemical interactions between the atoms and substrate molecules, but to the chemical fate of the reaction intermediates as well. Nucleogenic methods are also implemented within the program to investigate atom-molecule reactions of a different nature. Active areas of research include studies into the effect of kinetic energy on the quenching mechanisms for electronically excited nitrogen atoms, the stereochemical consequences of hot homolytic halogen atom substitution reactions, and the mechanisms of carbon atom reactions. [0.7 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Chemical Biodynamics Division **\$425,000**

15. *Artificial Photosynthesis*

Calvin, M.; Otvos, J.W.

Comm. 415-486-4321; FTS 451-4321

The project objective is to devise a synthetic system for storing the energy of visible light. The approach involves basic photochemical research in areas that will improve understanding of the relevant parts of such a storage system. First, there is a photoinduced electron-transfer process across a phase boundary, mimicking the natural photosynthetic process, followed by a stabilization of the initial electron-transfer products. These products are then catalytically converted to hydrogen and oxygen, the results of water photolysis, or to reduced organic compounds and oxygen if carbon dioxide is used as the substrate. For such an energy storage system to succeed, advancement must be made in two areas. (1) The quantum yield of the initial photochemical reaction must be improved. One method of improvement is to compartmentalize the oxidized and reduced products of the initial photoreaction in order to prevent back-reaction. Studies use flash photolysis to determine which reactions are limiting the achievable quantum yield. (2) Soluble catalysts must be found for the final conversion of the intermediate products on both sides of the electron-transfer assembly. For the oxidation side, the most attractive catalysts being studied are complexes or oligomers of transition metal elements,

which can exist in several oxidation states and might, therefore, be useful in the multielectron oxidation of water to oxygen. [2.6 FTE]

16. *Chemistry with Near-Infrared Photons*

Frei, H.

Comm. 415-486-4325; FTS 451-4325

Extension of the wavelength response of photochemical reactions of interest in solar photochemistry into the near-infrared spectral range is very important for substantial improvement of the use of the sun's energy for chemical purposes. The search for chemical reactions that can be initiated with these long wavelength quanta is the main goal of this work. Focus is on reactions that may serve as models, or suggest new concepts for chemical storage of near-infrared photons, their conversion into electrical energy, and use in photocatalysis and chemical synthesis. Controlled atom transfer reactions are explored in inert, cryogenic matrices by excitation of reactant pairs with red and near infrared light. Reaction paths are mapped by trapping of short-lived transients and elucidation of their structure by FT-infrared spectroscopy. Most recent examples are stereocontrolled photooxidation of alkenes and alkynes by red light excited nitrogen dioxide. These studies form the basis of controlled chemical synthesis with long wavelength solar light in a room-temperature matrix. Sensitive, time-resolved emission and absorption spectroscopy is used for the study of redox chemistry in aqueous solution. Most recent examples are reduction of singlet delta O₂ at a p-type Si electrode, and direct observation of the rise of one electron oxidation intermediate upon photooxidation of iodide at dye-sensitized TiO₂. The latter furnishes new insight into elementary reaction steps of halide oxidation at the semiconductor-solution interface. [2.1 FTE]

Chemical Sciences Division **\$160,000**

17. *Photochemistry of Materials in the Stratosphere*

Johnston, H.S.

Comm. 415-642-3674

This research is concerned with global change in the atmosphere, including photochemical modeling and experimental gas-phase photochemistry. In collaboration with Lawrence Livermore National Laboratory, theoretical studies are made of atmospheric transport, radiation balance, and photochemistry. Molecules of atmospheric interest are photolyzed, and the energies of the photofragmentation products are measured in molecular beams. [3.2 FTE]

Notre Dame Radiation Laboratory
University of Notre Dame
Notre Dame, IN 46556**Radiation Laboratory** **\$3,100,000****18. Organic Photochemical Processes***Chateauneuf, J.E.; Hug, G.L.*
Comm. 219-239-5458

Detailed mechanistic investigations of the interaction of light with organic materials, including photochemically induced organic reactions, are being performed using time-resolved spectroscopies. Photolytically generated reaction intermediates and electronically excited states are directly monitored by absorption and fluorescent techniques. The absolute kinetics and energetics obtained allow for mechanistic interpretation of such photochemical processes as photoinduced electron transfer, multiphoton ionization, photolytic bond cleavage, and photoinduced molecular rearrangements. Primary photolytic processes including geminate interactions of radical ions, solvated electron reactions, and protonation reactions are being probed by picosecond flash photolysis. Also, the detailed mechanisms of dissipation and storage of light energy by photogenerated organic intermediates are under investigation. Excited states of fluorescent radicals are being used to study spin-statistic restrictions on energy-transfer processes in solution. Electron and energy transfer in reduced dimensions are also being investigated to determine whether efficiency of reaction can be enhanced in strong local fields of polyelectrolytes. Additionally, a multifaceted investigation of molecular interactions in supercritical fluids (SCF) has been undertaken. Both time-resolved and steady-state techniques are being used to probe the molecular dynamics of SCF solutions and to evaluate possible reactivity enhancements in photochemically induced reactions. [4.2 FTE]

19. Quantum Mechanical Studies of Radiation-Produced Intermediates*Chipman, D.M.; Carmichael, I.C.; Bentley, J.*
Comm. 219-239-5562

Chemical properties of transient species, such as free radicals and molecules in excited states, are being characterized by modern methods of *ab initio* electronic structure theory to facilitate the interpretation of experimental studies of early processes following radiolysis or photolysis of various media. Contributions to spin densities from effects caused by spin polarization, electron correlation, and vibrational averaging are being evaluated to determine their relative importance in the observed magnetic hyperfine coupling constants for a variety of free radicals. The computational methods for this determination now have quantitative predictive power for simple inorganic and alkyl radicals and are being further developed and tested for application to larger conjugated systems. The geometries, energies, and vibrational frequencies of nitroso-alkane compounds are computed to elucidate experimental analysis of reactions occurring in spin-trap systems. Vibrational frequencies and intensities, measured by resonance Raman spectroscopy of transient free radicals, are being interpreted by calculation of the relevant ground-state force fields and excited-state geometry changes. This provides an explanation of the dramatic alterations in intensity patterns experimentally found at

different excitation wavelengths for various benzo-semiquinone and phenoxy radicals. Methods are being developed to compute autoionization lifetimes and branching ratios of highly excited electronic states when multiple decay channels are available. [2.6 FTE]

20. Inorganic Photochemical Processes*Ferraudi, G.J.*
Comm. 219-239-7676

The photochemical reactivity of coordination complexes, in electronic states that are not populated directly from the ground state, is investigated by using time-resolved sequential biphotonic excitations. In order to obtain comparisons between photoreactions initiated via monophotonic and sequential biphotonic irradiations as well as to characterize the excited states connected with such processes, these studies are carried out as a function of photon energy. Emphasis is placed on chemical systems with potential application to the photoreduction of CO₂ as a source of compounds (e.g., methanol, formaldehyde) which may function as fuels and/or important raw materials. Flash-induced time-resolved magnetic circular dichroism (TRMCD) spectra of long-lived excited states are determined to characterize upper electronic states usually associated with the photoreactivity in sequential biphotonic irradiations. TRMCD spectra of radicals and coordination complexes in unusual oxidation states is also utilized in the interpretation of corresponding electronic spectra. In addition, dynamic effects of magnetic fields on the luminescence and photochemical reactions of coordination complexes are investigated at intensities up to 90,000 Gauss. Magnetodynamic effects on the rates of redox reactions between carbon-centered radicals and coordination complexes are investigated and compared with those effects on the rates of inner-sphere and outer-sphere electron transfers between coordination complexes. [5.4 FTE]

21. Microwave Studies of Radiation-Produced Radicals*Fessenden, R.W.; Madden, K.P.*
Comm. 219-239-5354

The structures and reactivities of free radicals and excited states formed by radiolysis and photolysis are being studied by electron resonance (EPR), optical methods, and microwave absorption to determine the molecular and environmental factors controlling reaction rates and pathways. Definitive electronic and geometrical structures, including acid-base properties, come from EPR spectra and allow correlation with reactivity patterns. Rates of radical reactions are determined from EPR experiments using laser photolysis and pulse radiolysis. Electron spin polarization (CIDEP) defines electronic interactions and spin multiplicity during radical reactions. Considerable effort is currently given to measurements of the rates of spin trapping using a variety of radicals and spin traps. These data show a marked variation in trapping rate constants with radical nucleophilicity. Further work on structure-reactivity relationships will facilitate the design of better spin traps. The time dependence of microwave dielectric absorption by photochemical intermediates maps charge distributions to help explain variations in reaction mechanisms in solvents of varying polarity. Rates of rapid internal charge rearrangements in excited states are determined from the dispersive microwave signal. The yields, localizations, and decay kinetics of photoinduced

charge carriers in semiconductor particles and films are also measured by microwave absorption. [10.9 FTE]

22. Photochemical and Photoelectrochemical Processes for Energy Conversion

Kamat, P.V.

Comm. 219-239-5411

Ultrafast electronic processes following the bandgap excitation of colloidal semiconductor are characterized by time-resolved absorption and emission measurements to elucidate kinetics of electron and hole transfer, as well as factors that control charge-transfer efficiency. Efforts are being made to determine the role of surface modifiers (e.g., thio compounds) in controlling the size of semiconductor colloids in the quantum-size regime and in improving the selectivity and efficiency of photoelectrochemical processes. The effects of optical excitation intensity, wavelength, and temperature on the photophysical and photochemical behavior of quantized semiconductor colloids (e.g., metal oxides and metal sulfides) and coupled semiconductor colloids (e.g., $\text{TiO}_2\text{-CdS}$, ZnO-ZnS , and ZnO-ZnS-CdS) are investigated with picosecond and nanosecond laser flash photolysis. The kinetic and mechanistic details of the charge-injection process as well as the recombination of cation radicals with injected charge are investigated in a variety of semiconductor colloid (e.g., TiO_2 , ZnO) and dye systems. The behavior of excited states and photochemical transients in opaque particulate systems is characterized with front face emission and diffuse reflectance spectroscopy. These studies are directed toward improving the efficiency of photoinitiated redox events in organized molecular assemblies. [2.2 FTE]

23. Track Effects in Radiation Chemistry

LaVerne, J.A.; Mozumder, A.; Pimblott, S.; Schuler, R.H.

Comm. 219-239-5563

Experimental and theoretical methods are used to probe the radiation chemical effects of the track structure produced by ionizing radiation. Experimental studies currently concentrate on the heavy-ion radiolysis of liquid hydrocarbons. In these studies the dependences of product yields and luminescence on particle charge, energy, and linear energy transfer (LET) are compared with those found in fast electron radiolysis. Measurements using a wide variety of particles with energies up to 15 MeV/nucleon and which exhibit LETs of 10 to 4000 eV/nm are being carried out at the heavy-ion accelerators of the Notre Dame Nuclear Structure Laboratory as well as the Argonne Tandem/LINAC Accelerator Systems (ATLAS) facility of Argonne National Laboratory. Theoretical models based on experimentally determined inelastic and ionization cross sections are being developed in order to estimate the distributions of ionization, excitation, and primary species in both fast-electron and heavy-ion tracks. These theoretical models use stochastic and deterministic approaches to examine the various competitions within tracks in alkanes, aqueous solutions, and aromatic crystals. Experimental and theoretical methods are also employed to study luminescence quenching in liquefied rare gases irradiated with heavy ions and electrons. [6.2 FTE]

24. Influence of Ordered Molecular Assemblies on Photochemical Processes

Patterson, L.K.

Comm. 219-239-5403

The chemistry of excited states and free radicals in organized molecular systems is investigated to determine the effects of reduced dimensionality, molecular orientation, and interfacial parameters on reaction mechanisms. Determination of the means by which molecular organization may be used to exercise kinetic control over reactions of interest is a principal goal of this work. Particular attention is given to processes related to solar energy storage. While micelles, vesicles, and Langmuir-Blodgett films are utilized in these studies, efforts are focused on chemistry in spread lipid monolayers at the gas-water interface. With these systems it is possible to both monitor and alter the degree of molecular organization with a high level of control. Time-resolved and steady-state fluorescence are used to measure energy transfer, self quenching, diffusion, monolayer permeability, and interfacial polarity as functions of layer organization. Steady-state photochemical reaction products from reactions at the water surface are analyzed by high-performance liquid chromatography (HPLC) techniques. Auxiliary tools, such as surface conductivity, are used to characterize lipid headgroup behavior in the interfacial region. While not practical in monolayers, flash photolysis and pulse radiolysis measurements can be carried out in micellar systems to characterize effects of the microenvironment on behavior of triplet excited states and of lipid radicals. [5.4 FTE]

25. Radiation Chemistry Data Center

Ross, A.B.; Helman, W.P.; Hug, G.L.; Carmichael, I.C.

Comm. 219-239-6528

Kinetic, spectroscopic, and thermodynamic data for processes in solution involving reactive intermediates, including free radicals and excited states, are being evaluated and collected into databases. Photophysical properties of excited singlet and triplet states of organic and inorganic molecules in condensed phase are being compiled, including kinetic data for first-order decay and bimolecular quenching reactions. The broad range of properties includes quantum yields, energy levels, absorption spectral parameters, and lifetimes. A current compilation project covers quantum yields for the photosensitized production of singlet molecular oxygen. A database on free-radical kinetics for transient radicals, produced in the radiolysis or photolysis of fluid solutions, has been assembled and additional data are being added. Scientists from other laboratories collaborate in the compilation and evaluation of these data. The evaluated data are disseminated in published tables and by electronic means. The Radiation Chemistry Data Center (RCDC) provides on-line access to numeric databases covering (1) rate constants for about 6900 reactions involving inorganic radicals in aqueous solution, (2) triplet-triplet absorption spectral data for over 1100 organic molecules in condensed phases, and (3) the RCDC Bibliographic Database (RCDbib). RCDcbib contains over 117,000 references and is used to produce the current-awareness publication, "The Biweekly List of Papers on Radiation Chemistry and Photochemistry." [4.7 FTE]

26. Radiation-Induced Chemical ReactionsSchuler, R.H.; Tripathi, G.N.R.; Patter-
son, L.K.

Comm. 219-239-7502

The behavior of radicals produced by oxidation, reduction, and electron-transfer reactions in aqueous systems is being studied by time-resolved absorption and resonance Raman methods. Recent experiments have largely focused on prototype organic sulfur-containing radicals produced radiolytically from thioaromatics and on simple inorganic radicals such as $O_2^{\cdot -}$. Raman studies, which are unique to this laboratory, provide structural information on a variety of important reaction intermediates and allow the reaction kinetics of these intermediates to be examined where spectral overlap obscures kinetic spectrophotometric experiments. Combined pulse-radiolysis and flash-photolysis methods are used to examine photochemical properties of short-lived intermediates produced radiolytically. Information on product distribution obtained by chromatographic methods is integrated with that from time-resolved studies of the intermediates to give a detailed picture of the attack of OH radicals on aromatic systems. Scavenger methods are being developed to provide data on the lifetime distribution of primary radiolysis products in electron tracks, with the aim of using these methods to examine the competitive processes in the tracks of heavy particles. Product studies with high-intensity pulses also provide important information on the competition between second-order reactions of radicals and electron-transfer processes. [9.0 FTE]

28. Surface-Modified Semiconductor Electrodes for Solar Photochemical Energy Conversion

Frank, A.J.

Comm. 303-231-1962; FTS 327-1962

The photoelectrochemical properties and charge-generation mechanism of conductive polymers, the optical and electrical characteristics of the polymer-semiconductor junction, and chemically derivatized semiconductor particles are being investigated. The charge carriers and band structure that evolve upon doping of electrochemically grown poly(3-methylthiophene) (PMeT) films were extensively characterized as a function of their preparation conditions by optical absorption, infrared, and electron spin resonance measurements. Current-voltage, capacitance-voltage, optical absorption, and electron beam-induced conductivity (EBIC) measurements were utilized to elucidate the thermodynamic and kinetic factors limiting the conversion efficiency of the junction formed between undoped p-PMeT and n-CdS. Fundamental processes controlling the photoelectrochemical behavior and the photostability of PMeT are also under investigation. Work continues on the study of the first example of a molecular water-reduction catalyst for chemically derivatizing TiO_2 colloids and powder suspensions. The catalyst, which is formed *in situ* by direct optical excitation of TiO_2 in the presence of $[Pt(bpy)_2]^{2+}$, exhibits considerably higher activity for H_2 evolution than elemental platinum on TiO_2 particles. [2.8 FTE]

**Solar Energy Research Institute
Golden, CO 80401****Fuels and Chemicals Research \$1,245,000
and Engineering Division****27. Photophysics and Photochemistry of Porphyrin Systems and Photosystem II Reaction Centers**

Connolly, J.S.; Seibert, M.

Comm. 303-231-1873; FTS 327-1873

This project focuses on fundamental aspects of light-induced electron transfer in molecular systems leading to the design and assembly of a synthetic photoreaction center. To date, the work has concentrated on electron-transfer interactions in porphyrin-containing molecular assemblies. Current investigations are concerned with tightly linked porphyrin-quinone molecules in which strong electronic coupling between the donor and acceptor moieties is highly sensitive to small changes in the dielectric properties of the host matrix. Local environments are probed in various media, including liquid mixtures, vesicles, and polymers. Studies are being carried out on the temperature dependence of charge-transfer interactions by steady-state measurements of the emission spectra, picosecond measurements of the kinetics and, where possible, time-resolved optoacoustic measurements of the energetics. The goal is to understand the specific properties of protein membranes that facilitate electron transfer *in vivo* and to stabilize the resulting redox products. Electron transfer and primary charge separation functions are also under investigation in isolated antenna and photosystem II reaction center complexes. [2.4 FTE]

29. Quantization Effects in Photoelectrochemistry

Nozik, A.J.; Turner, J.A.

Comm. 303-231-1953; FTS 327-1953

Fundamental aspects of quantization effects in multiple quantum wells, single quantum wells, superlattices, and quantum particles (in the form of colloids) are being investigated in the context of photoelectrochemical problems and issues. Time-resolved hot photoluminescence experiments in the femtosecond and picosecond regime have resolved an important controversy by unequivocally showing that the rate of hot electron cooling in quantum wells is much greater than in bulk semiconductors at high photocarrier densities. Studies of the temperature dependence of photocurrent action spectra and I-V data show that electron tunneling dominates electron transfer from quantum well electrodes with 20 Å barriers, while thermionic emission is controlling in quantum wells with thicker barriers. Advances have been made in synthesizing neat, quantized particles of important semiconductors, such as GaAs, which has not been produced previously without interfering moieties. Measurements of the rates of electron transfer vis-a-vis electron relaxation are being measured for both quantum films and quantum particles. Novel applications of quantized structures to basic problems in photoelectrochemistry are also being pursued. [6.9 FTE]

Chemical Physics

Ames Laboratory
Iowa State University
Ames, IA 50011

Fundamental Interactions Program **\$705,000**

30. Chemical Theory
DePristo, A.E.
Comm. 515-294-9924

The general focus of this research is the theoretical description of the structure and dynamics of chemically reactive systems in terms of their fundamental atomic and electronic constituents. Research is designed to describe, calculate, predict, and understand properties of such unusual chemical systems as metal and semiconductor clusters. The goal is to determine the structure and energy of various clusters, and to investigate the relationship between these properties and the reactivity of clusters with different gas-phase molecules. First principle, *ab initio* and semiempirical quantum mechanical electronic structure techniques are utilized along with classical dynamics. Another effort involves analysis of the kinetics and nonequilibrium structure associated with irreversible or far-from-equilibrium adsorption and catalytic reaction processes on solid surfaces. The goal is to understand the interplay between kinetics and structure. [2.0 FTE]

31. Molecular Beam Photoionization and Photodissociation Studies of Molecules, Clusters, and Radicals
Ng, C.Y.
Comm. 515-294-4225

The project objectives are (1) to provide accurate thermochemical data for molecules, clusters, radicals, and molecular ions and (2) to study the mechanisms and dynamics of elementary chemical processes relevant to combustion chemistry. A new photoion-photoelectron coincidence (PIPECO) technique has been developed that makes possible the measurement of the photoelectron spectrum (PES) of minor species with concentrations less than 1% of a gaseous mixture. The PIPECO method is ideal for measuring the PES of radicals because radicals are usually generated by discharge, reaction, or pyrolysis in mixtures with their precursors. A project to systematically measure the PIPECO spectra of radicals related to combustion is currently under way. A supersonically cooled laser photodissociation radical beam source has been developed. This source will allow accurate ionization energy measurements of polyatomic radicals. Another area of interest involves the study of the excimer laser photofragmentation dynamics and energetics of a series of sulfur-containing compounds and their clusters. In addition to information about the internal energy distributions of photofragments, these experiments will provide reliable estimates of the C-S and S-S bond energies of these compounds. [3.75 FTE]

32. Molecular Bonding Theory
Ruedenberg, K.
Comm. 515-294-5253

Fundamental nonempirical quantum mechanical theory is used to determine properties of molecules and chemical reactions. Since the unifying concept for the understanding of molecular structure and dynamics is the molecular energy surface, a major objective is the global mapping of such surfaces by accurate *ab initio* calculations as functions of the atomic positions, and the determination of those critical surface features that determine directions and rates of chemical reactions. The resulting predictions of reaction paths, transition states, reaction energies, activation energies, and unstable intermediates provide information that, in most cases, is inaccessible by nontheoretical means. In this context, methods for calculating many-electron molecular wave functions are developed that include the correlations between electronic motions required for yielding the pertinent relative energy changes with sufficient accuracy. Because most distinctive energy surface modulations, such as minima, saddles, valleys, bifurcations, and surface crossings, cannot be simply rationalized, rigorous explanations in terms of electronic rearrangements are needed. Consistent general methods are therefore developed for an in-depth analysis of *ab initio* electronic wave functions, leading to relations between energetic interactions and electronic rearrangements. Oxidation-reduction reactions, exchange reactions, and isomerizations relevant to combustion, hydrogenation, or atmospheric problems are investigated. Currently, global potential energy surfaces are being established for the O_3 molecule. [2.25 FTE]

Argonne National Laboratory
Argonne, IL 60439

Chemistry Division **\$3,913,000**

33. Photoionization-Photoelectron Research
Berkowitz, J.
Comm. 708-972-4086; FTS 972-4086

The vacuum ultraviolet photoionization of atoms, free radicals, and small molecules is studied at high photon resolution. The transient species are prepared *in situ* by pyrolysis, electrical discharge, chemical reaction, or laser photolysis. The ongoing studies of atoms are revealing systematic behavior in the breadth and shape of autoionizing lines, which can be rationalized with a simple theory even though it is inherently a complex, many-body phenomenon. With molecules, a persistent ionization below the known ionization threshold has been examined, and attributed to rotational autoionization in several molecules. The characteristics of this process (e.g., dependence on electric field, dipole moment) are being studied. The free-radical studies are currently providing accurate thermochemical information on important intermediates in combustion reactions, such as C_2H_3 , C_2H_5 , CH_3O , CH_2OH , and the previously undetected $COOH$. An important contribution to combustion studies was the determination of DH_f° (C_2H) and D_0 ($HCC-H$). Studies are in progress on the Si_2H_n system. Unlike their carbon analogs, Si_2H_4 and Si_2H_2 previously had not been observed. Preliminary data indicate that the bonding in silicon hydrides is drastically different from the isovalent carbon hydrides, e.g., the

ground state structure of Si_2H_2 is cyclic (doubled bridged), unlike the triple bonded C_2H_2 . These studies will provide thermochemical information on the Si_2H_n species and their cations, essential for modeling the kinetics of silane plasmas used in thin-film technology. Conventional He and threshold photoelectron spectroscopy are used to measure the spectroscopic properties of atomic and molecular ions. Another apparatus is used to study directly the spectroscopy and dynamics of molecular-ion decomposition by analyzing the fragments ensuing from ultraviolet laser irradiation of selected molecular ions. One recent application of this device is to distinguish clearly between isomeric molecular ions. [4.0 FTE]

34. *Metal Cluster Chemistry Research*

Riley, S.J.; Parks, E.K.; Jellinek, J.; Knickelbein, M.B.

Comm. 708-972-6793; FTS 972-6793

The chemical and physical properties of isolated transition-metal clusters are studied. Clusters of from two to several hundred atoms are generated by pulsed lasers and detected by laser-ionization mass spectrometry. Metals studied include iron, cobalt, nickel, niobium, aluminum, chromium, vanadium, rhodium, titanium, copper, and platinum. Chemical properties are studied in a unique continuous gas-flow-tube reactor. The dependence of cluster reactivity on size is determined and shows correlation to other chemical and physical properties. Adsorbate uptake patterns are measured and give information about cluster structure, changes in structure with cluster size, and the nature of adsorbate binding sites. Adsorbate binding energies are measured and are compared to those of the bulk metal. Mechanisms for adsorbate decomposition on cluster surfaces are characterized. In another apparatus, cluster physical properties such as ionization potentials, electron affinities, and photo-physical processes are probed. These experimentally determined cluster properties are correlated with theoretical calculations. Additional theoretical effort is aimed at developing tools for studying cluster dynamics and chemical reactions on cluster surfaces. Ultimately, these studies will provide a better understanding of surface chemistry and heterogeneous catalysis. [8.2 FTE]

35. *Chemical Dynamics in the Gas Phase*

Wagner, A.; Davis, M.; Harding, L.; Harrison, R.; Shepard, R.; Liu, K.; MacDonald, R.;

Michael, J.; Hessler, J.; Gray, S.

Comm. 708-972-3597; FTS 972-3597

The project mission is to characterize by advanced theoretical and experimental techniques the inelastic and reactive properties of small molecules and radicals in the gas phase, with an emphasis on those species of importance in combustion chemistry. The theoretical effort applies advanced electronic structure methods to the calculations of spectroscopic force fields, reaction paths, and entire potential energy surfaces. These results are then used in statistical, trajectory, or advanced quantum dynamics calculations to obtain cross sections and rate constants for comparison to experiment. Because these applications are so computer intensive, substantial effort is devoted to a project to develop portable chemistry codes optimized for cost-effective parallel computing architectures. The experimental effort involves: (1) radical-molecule rate

constant measurements in shock tubes at low temperatures (flash- or laser-photolysis-resonance-absorption) or high temperatures (laser-flash absorption) and (2) state-resolved cross section measurements of radical-molecule scattering with crossed, pulsed molecular beams and laser spectroscopic detection. A new project directed at the measurement, in a flow tube, of the state-resolved product distribution for radical-radical reactions is in the construction phase. [17.1 FTE]

Brookhaven National Laboratory Upton, Long Island, NY 11973

Department of Applied Science

\$580,000

36. *Combustion Kinetics and Reaction Pathways*

Klemm, R.B.; Sutherland, J.W.

Comm. 516-282-4022; FTS 666-4022

This project is focused on the fundamental chemistry of combustion. The overall objectives are to determine rate constants for elementary reactions and to elucidate the pathways of multichannel reactions. A multitechnique approach that features three independent experiments provides unique capabilities in performing reliable kinetic measurements over an exceptionally wide range in temperature, 300 to 2500 K. Some recent kinetic studies include: $\text{O} + \text{H}_2\text{O}$ (1050 to 2030 K), $\text{O} + \text{C}_2\text{H}_6$ (400 to 1400 K), $\text{H} + \text{CH}_4$ (900 to 1700 K), and $\text{CH}_3 + \text{Ar}$ (thermal decomposition of methane, 1700 to 2150 K). A discharge flow-photoionization mass spectrometer (DF-PIMS) experiment is used to identify primary products from multichannel reactions, to determine photoionization spectra for reactants and products, and to measure ionization potentials of free radicals. The DF-PIMS apparatus was designed to be operated on the U-11 beamline at the National Synchrotron Light Source (NSLS) and thus take advantage of tunable vacuum ultraviolet light to improve detection sensitivity and selectivity in monitoring free radicals. A recent result from the DF-PIMS studies is the determination of the branching ratio for the two CH_3 -forming channels of the $\text{O} + \text{C}_3\text{H}_6$ reaction. Also, the dissociative ionization of vinoxy radical, to form CH_3^+ and CO , was confirmed by direct observation. [4.7 FTE]

Chemistry Department

\$2,835,000

37. *Energy Transfer Studies in Cluster Impacts*

Friedman, L.; Friedlander, G.; Beuhler, R.J.

Comm. 516-282-4325; FTS 666-4325

The impacts of accelerated cluster ions on solid surfaces generate transient, highly compressed assemblies of energetic atoms. These assemblies are unique in that very large amounts of energy are concentrated in the motion of the atoms rather than in excitation of the electrons, so that cooling processes are slower than in systems heated by lasers, electron beams, or high-velocity ion beams. The direct deposition of energy into the motion of target atoms produces a nonrandom directional distribution of translational energy in the target atoms. As a consequence, a very small fraction of the target atoms may acquire sufficient translational and/or vibrational energy to drive

nuclear fusion reactions. A study of the effects of cluster impacts on solid surfaces in economical, laboratory-scale experiments can illuminate mechanisms of the ablative processes normally relied upon to compress and heat plasmas in inertially confined fusion. In addition, the direct application of cluster beams in place of heavy-ion beams to heat inertially confined plasmas can be investigated. Most of the proposed experimental work will build on the foundation already established in studies of fusion reactions induced by singly charged accelerated cluster ions. New studies will focus on the exploitation of multicharged ions to extend the range of velocities and sizes of the projectiles used to initiate cluster-impact phenomena. The major objectives of this project are to study the properties of condensed matter under extreme conditions of pressure and energy density, and to evaluate the potential of cluster impacts for use in the economical development of fusion energy. [3.1 FTE]

38. Gas-Phase Molecular Dynamics

Weston, R.E.; Muckerman, J.T.; Sears, T.J.;
Preses, J.; Hall, G.E.
Comm. 516-282-4373; FTS 666-4373

Research in this project explores the energetics and dynamics of molecular collision phenomena and the microscopic factors affecting the structure and dynamics of short-lived intermediates in gas-phase chemical reactions. Both experimental and theoretical techniques are directed toward the study of the spectra of small free radicals, and of state-to-state dynamics of gas-phase collision, energy-transfer, and photodissociation phenomena. The objective is a fundamental understanding of transient species and chemical processes, especially those related to combustion. Experimental tools include diode laser absorption; pulsed excitation using infrared, visible or ultraviolet lasers or ultraviolet synchrotron radiation; laser-induced fluorescence and stimulated emission pumping; time-resolved Fourier transform infrared detection of excited species; and time-resolved fluorescence studies. These are augmented by theoretical studies in which quasi-classical, semiclassical, and quantal methods, particularly those combining classical and quantal wavepacket descriptions for different degrees of freedom, are developed and applied to prototypical chemical systems. Since the merging of the scientific programs previously on beam lines U9A and U11 at the National Synchrotron Light Source, this program provides assistance to some of the outside users of beam line U11. [10.0 FTE]

39. Gas-Phase Photoionization of Molecules and Molecular Complexes

White, M.; Grover, J.R.; DiMauro, L.
Comm. 516-282-4345; FTS 666-4345

The general aim of this program is the experimental characterization of optically prepared excited and ionic states of molecules and molecular complexes and their nonradiative decay dynamics. Intense synchrotron and laser radiation sources are used to induce excited neutral or ionic state processes such as dissociation, dissociative rearrangement, and autoionization, the products of which are probed by a variety of photoionization-based techniques. Particular emphasis is placed on elucidating the decay dynamics of neutral or ionic molecular species with high internal energy content. For isolated molecules,

these studies focus on state-resolved measurements of dissociation dynamics in the vacuum ultraviolet (VUV) and rotationally resolved photoionization studies using novel threshold photoelectron techniques. Parallel investigations of weak molecular complexes are aimed at obtaining mechanistic and dynamical information on dissociative rearrangement processes of molecular intermediates produced by photoionization. Time-resolved fluorescence studies are aimed at probing the structure and dynamics of "cold" chemically transient species. Studies of the effects of high-intensity laser fields on simple, isolated systems are also under investigation with the ultimate goal of controlling modified collision dynamics for physical and chemical processes. [4.0 FTE]

**Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720**

Applied Science Division

\$175,000

40. Combustion Chemistry

Brown, N.J.
Comm. 415-486-4241; FTS 451-4241

Combustion processes are governed by chemical kinetics, energy transfer, transport, fluid mechanics, and the complex interactions among these. In all chemical changes, the pathways for energy movement and the competition among the pathways determine reaction rates, product yields, and product state energy distributions. Understanding the fundamental chemical processes offers the possibility of optimizing combustion processes. Recent research has been concerned with the application of functional sensitivity analysis to determine the relationship between dynamic observables and the potential energy surface structure. This provides an understanding of how different regions of the potential play a part in controlling the dynamics, and thereby influence the eventual outcome of calculated observables. Functional sensitivity analysis has been applied to classical dynamics studies of energy transfer and to quantum mechanical studies of reactive scattering. Functional sensitivity analysis can be used to identify regions of configuration space of highest sensitivity so that quantum chemists calculate a high density of *ab initio* points in those regions, and the full sensitivities can be used in guiding the improvement of the potential surface to obtain better agreement between theory and experiment. A second portion of the effort is concerned with modeling combustion chemistry with particular emphasis on the use of parametric sensitivity analysis. [1.0 FTE]

Chemical Sciences Division

\$2,560,000

41. Energy Transfer and Structural Studies of Molecules on Surfaces

Harris, C.B.
Comm. 415-642-2814

The goal of this research is to study the dynamics of excited electronic states on surfaces, at interfaces, and in condensed phases and to develop new laser techniques for studying these dynamics. The research program is both theoretical and experimental in character, and includes

nonlinear optical and ultrafast laser techniques in addition to a variety of standard surface science tools for characterizing surfaces and adsorbate-surface interactions. Recent work has centered on the development of new techniques for studying the dynamics of electrons at interfaces on femtosecond time scales, carrier diffusion in semiconductors, and photodissociation of transition metal carbonyls in solution. The results of this program have a direct bearing on high-speed technological devices and materials, and on other problems of general interest such as the dynamics of electrical transmission in conductors on ultrafast time scales and the optical properties of thin films. [2.0 FTE]

42. *Chemical Dynamics*

*Lee, Y.T.; Lester, W.A.; Miller, W.H.;
Moore, C.B.; Kung, A.H.; Neumark, D.
Comm. 415-486-6154; FTS 451-6154*

The objectives of this program are to develop the basic knowledge and understanding of the mechanisms and dynamics of elementary chemical reactions that have major impact on combustion and advanced energy production technologies. Recent emphasis has been to determine the structure and chemical behavior of free radicals, unusual transient species, clusters and cluster ions, and highly excited polyatomic molecules, and to provide microscopic details of primary photodissociation and bimolecular processes. These objectives are achieved with a strongly coupled experimental and theoretical-computational approach using cutting-edge methodologies. Dynamical studies use advanced molecular beams and photofragmentation spectroscopy. Kinetics studies employ infrared (ir) laser flash kinetic spectroscopy and high-resolution ultraviolet-vacuum ultraviolet (UV-VUV) laser spectroscopy. New theoretical methods and models are developed both to provide insight into chemical reactivity and the dynamics of reactive processes and also to allow one to carry out forefront calculations to guide and model variations of these experimental studies. Advanced tools such as an infrared free-electron laser and synchrotron light source instrumentation are being developed for the next generation experiments which require the settings of a major facility. [17.8 FTE]

43. *Physical Chemistry with Emphasis on Thermodynamic Properties*

*Pitzer, K.S.
Comm. 415-642-3472; FTS 451-5456*

The purpose of this project is the discovery and development of methods of calculation of thermodynamic and related properties of important chemical systems by use of quantum and statistical mechanics together with experimental measurements for key systems. Particular attention will be directed to the development of theoretically guided equations of state for mixed fluids with components of widely different molecular type and unlimited number. The inclusion of ionic components introduces special problems because the alternating charge and long-range nature of ionic forces require a separate theoretical treatment. A recent contribution was the set of precision near-critical measurements on a liquid salt, polar solvent system that provided for the first time the critical exponent β of an ionic system. The critical exponents for ionic fluids are a matter of current controversy theoretically. Other recent contributions have related to the properties

at very high temperature and pressure of aqueous NaCl and KCl. Systems dominated by these salts but containing additional components are of both geological and industrial importance. In connection with research in this area, there is liaison and/or collaboration with other Department of Energy (DOE) or United States Geological Survey (USGS) groups as appropriate. [1.5 FTE]

44. *Chemical Physics at High Photon Energies*

*Shirley, D.A.
Comm. 415-486-7633; FTS 451-7633*

This project is focused on the future utilization of the Advanced Light Source, now under construction at the Lawrence Berkeley Laboratory, for research in chemical physics. Two major goals are (1) the performance of path-breaking research based on high-brightness vacuum ultraviolet radiation and (2) the training of chemistry Ph.D. students in synchrotron radiation science. Research projects are identified to emphasize those priority research areas that are amenable to study with vacuum ultraviolet radiation: chemical reactivity, chemical catalysis, and matter under extreme conditions. Effects are emphasized that can be refined and extended with the advent of third-generation light sources (e.g., angular distribution effects in threshold and near-edge photoexcitation phenomena, very fast processes, and processes requiring very high intensity and energy resolution). Electron correlations in atoms and molecules are studied, especially in the adiabatic (low-energy) limit, where the electronic structure of the continuum is important. Molecular-beam angle-resolved time-of-flight spectroscopy is performed, using supersonic beams. Surface structures are also studied using photoelectron diffraction in the variable energy mode, and observing angle-resolved photoemission extended fine structure (ARPEFS). In fact, development and extension of the ARPEFS method, which is complementary to surface extended X-ray absorption fine structure (EXAFS) and other surface structural tools, is a major activity of this project. [9.25 FTE]

Lawrence Livermore National Laboratory University of California Livermore, CA 94550

Division of Computational Physics **\$40,000**

45. *Chemical Kinetics Modeling*

*Westbrook, C.K.
Comm. 415-422-4108; FTS 532-4108*

This project consists of computer modeling of chemical kinetics of combustion of hydrocarbon and other fuels. Of particular interest are fuels that are used in practical energy conversion systems, including internal combustion engines, burners, and gas turbines. Current topics of attention in this program address the roles played by fuel molecular structure and size in determining combustion properties such as oxidation rate, pollutant emissions, and relative ignition rates. Isomers of pentane, hexane, and heptane are being used to determine the importance of bond locations and strengths on knocking tendency and

octane number in internal combustion engines. This project is also investigating the manner in which oxygenated hydrocarbon species influence ignition of other hydrocarbons, with particular attention to known anti-knock compounds such as methyl-tert-butyl ether (MTBE). Modeling is being extended to chlorinated hydrocarbons, including many species identified as contributors to toxic and hazardous industrial wastes. In all cases, model calculations are used to determine those reactions whose rates and products have particularly strong influences on the overall rates of combustion and which require further attention. [0.3 FTE]

Pacific Northwest Laboratory Richland, WA 99352

Molecular Science Research Center \$3,000,000

46. *Chemical Structure and Dynamics* Colson, S.D. Comm. 509-375-6882

The Chemical Structure and Dynamics program responds to the need for a fundamental molecular level understanding of chemistry at environmental interfaces. The research is built around the established relationship between structure and function (reaction dynamics) that is the underpinning of molecular science. The structural studies are key to the direct comparison with theory. Real time dynamics measurements of atomic/molecular motions during chemical reactions provide for a molecular level description of reaction dynamics. One program element relies upon the synthesis and characterization of microscopic models of condensed phase chemistry. Atomic and molecular clusters are a form of matter whose properties lie outside the realm of general chemical experimental science. They not only provide a quantitative basis for comparison with theory but are the source of a microscopic understanding of the condensed phase. Another initiative brings a combination of state-of-the-art lasers and atomic resolution surface mapping tools (i.e., scanning tunneling microscopy (STM)) to the study of interfacial chemistry. The combination of lasers and surface mapping tools allows direct observation of reactions on realistic chemical surfaces. The cluster and surface science initiatives illustrate two elements of a broad program including structure and dynamics studies of molecules in isolation, condensed in microstructures, in solution, and on extended surfaces. [9.6 FTE]

47. *Molecular Theory and Modeling* Dunning, T.H., Jr. Comm. 509-375-6863

The molecular theory and modeling project is designed to provide a molecular-level understanding of molecular processes in the atmospheric, terrestrial, and subsurface environments. This knowledge is critical to the development of reliable models of contaminant transport and transformation in the air, groundwater, and soil. To achieve this goal, the project is focused on theoretical and computational studies of molecular processes in isolation (gas phase) and in liquids, on surfaces, and at interfaces (condensed phases). The research objectives of the project

are (1) application of *ab initio* techniques to study elementary molecules processes important in the environment; (2) extension of *ab initio* techniques to treat molecular systems of environmental importance; (3) modeling molecular processes in the multispecies, multiphase systems prevalent in the environment; and (4) development of accurate modeling techniques for describing complex environmental molecular systems. Specific areas of current research interest include: the reactions of sulfurous species in the atmosphere; the solvation of ions, reaction of hydroxyl anion, and dynamics of twist-induced charge transfer processes in solution; and the modeling of substrate-mineral surface interactions in soils. [6.9 FTE]

Sandia National Laboratories, Livermore Livermore, CA 94551-0969

Combustion Research Facility \$2,400,000

48. *Combustion Research Facility (CRF) Diagnostics Research: Coherent Raman Processes* Lucht, R.P.; Farrow, R.L.; Rahn, L.A. Comm. 415-294-3089; FTS 234-3089

This project develops coherent Raman diagnostic techniques in support of Combustion Research Facility (CRF) programs. Detailed studies are made of processes affecting coherent anti-Stokes Raman spectroscopy (CARS), a leading technique for time-resolved measurements of temperature and major species concentrations. Processes studied recently include collisional broadening, Doppler broadening and narrowing, collisional reorientation of rotational alignment, saturation, and elastic vibrational dephasing. In particular, a new theory, based on speed-dependent collisional shifts, has been developed to account for asymmetric inhomogeneous line shapes observed in hydrogen. A high-resolution CARS system is used to examine saturation of Doppler-broadened line shapes, to perform pump-probe experiments for measuring inelastic rotational state-to-state transfer rates directly in nitrogen and hydrogen, and to measure high-temperature linewidths in high-pressure lamps. The modification of CARS spectra at high pressure caused by collisional narrowing is quantified in detail using high-resolution CARS and high-resolution inverse Raman spectroscopy, so that measurements in high-pressure environments (e.g., internal combustion engines) can provide more accurate results. Inverse Raman spectroscopy is also used to develop a high-resolution database of spectral parameters for important combustion species such as nitrogen, carbon monoxide, hydrogen, and water vapor. A computer code for analyzing CARS spectra and for determining temperatures and concentrations is maintained and upgraded to incorporate advancements in spectral models. This project is supported with facility operations funds. [5.0 FTE]

49. Combustion Research Facility (CRF) Diagnostics Research: Advanced Methods

Lucht, R.P.; Goldsmith, J.E.; Koszykowski, M.L.; Rakestraw, D.J.; Trebino, F.P.
Comm. 415-294-3089; FTS 234-3089

This project supports the development and theoretical interpretation of new, nonlinear, laser-based techniques for detecting trace species and for studying resonant wave-mixing processes in combustion environments in support of Combustion Research Facility (CRF) projects. Absolutely calibrated profiles of hydrogen atoms in hydrogen/oxygen and hydrocarbon flames have been obtained. Photochemical effects as a source of interference in measurements of hydrogen and oxygen atoms in flames have been identified. Stimulated emission following multiphoton excitation of flame radicals is currently under investigation. Temperature measurements and imaging of OH, CH, and NO have been achieved using a promising new combustion diagnostic, degenerate four-wave mixing. Rapid progress has been made in the development of ultrafast pulse (on the order of 50 femtoseconds) optical techniques for the study of chemical dynamics processes. In the area of theoretical studies, resonant wave-mixing spectra are calculated using both perturbative and non-perturbative solution of the fundamental density matrix equations. Three-level models have been developed and calculations performed to understand the many processes affecting transient femtosecond excite-probe experiments, including saturated absorption, free-induction decay, coherent artifacts (transient gratings), perturbed free-induction decay, photon echo, accumulated photon echo, orientational relaxation, and probe-beam saturation. A model has been developed to determine ultrafast laser pulse widths, self-phase modulation, and chirp from measurements based on induced thermal gratings. Such measurement techniques are more robust than second-harmonic generation or autocorrelation techniques. This project is supported with facility operation funds. [4.0 FTE]

50. Flame Chemistry: Modeling and Experiments

Miller, J.A.; Kee, R.J.; Durant, J.L.; Fisk, G.A.
Comm. 415-294-2759; FTS 234-2759

The goal of this research is to determine the predominant chemical reactions that transform reactants to products in flames. Much of the work focuses on pollutants. A recent, exhaustive study of nitrogen's combustion chemistry has led to a kinetic model that predicts quantitatively the formation and destruction of nitrogenous pollutants under a wide variety of conditions. Current emphasis is on the chemistry of carbon-containing species in rich oxygen/acetylene flames, particularly the reactions that form soot precursors. Recent experiments and modeling have led to improved understanding of the growth of higher hydrocarbons and the formation of aromatic rings. Low-pressure flame experiments use laser diagnostics to yield temperature and the concentration profiles of radicals such as OH, CH, and H. Mass-spectrometric techniques give concentrations of stable species in the flames. A crucial element of the work is extensive modeling using computer programs that include transport phenomena and chemical kinetics. The recently extended model now predicts the major features of lean to lightly sooting acetylene/oxygen

flames. In addition to studying laminar flames, this research is developing computational techniques for treating turbulent combustion. Present research is developing a chemical kinetics model for turbulent jet flames. [4.0 FTE]

51. Turbulent Reacting Flow Research

Schefer, R.W.; Sweeney, D.W.; Barlow, R.S.; Paul, P.H.; Chen, J.-Y.; Chen, J.H.
Comm. 415-294-3138; FTS 234-3138

This research is directed toward an increased understanding of the coupling and competition between the chemical kinetic and mixing processes in turbulent reacting flows. This research project features close coupling between theory and experiment. The turbulent jet flame experiment is the simplest configuration of nonpremixed reactants that retains the fundamental ingredients of chemical reaction and turbulence. By adjusting velocities or by changing reactants, an important range of chemical kinetic and mixing rates can be explored. The mixing rates and chemical kinetic rates are quantified by using simultaneous multi-species laser Raman scattering and OH laser-induced fluorescence from which major species concentrations, temperature, and OH concentration are obtained on each laser pulse. The OH radical concentration is an excellent measure of the degree of chemical nonequilibrium in the flow. Ensembles of these measurements are directly compared with predicted ensembles of data from Monte Carlo numerical modeling of this flow. The Monte Carlo calculations of probability density functions are performed using the Sandia CRAY X-MP supercomputer. A major focus of the numerical efforts is the incorporation of reduced chemical kinetic schemes in turbulent flame codes. Chemical kinetic and mixing interactions in the more complicated flow configuration of the bluff-body flame are also being explored. Quantitative images of fuel concentration and fuel zone structure have been obtained from simultaneous, two-dimensional imaging of CH and methane. These images have allowed a critical comparison of the predictions of two different models of combustion: the flamelet and dissipative-eddy models. The experimental data are predicted more accurately by the dissipative-eddy model. OH imaging measurements in these flows have recently been performed as well as simultaneous CH, methane, and OH imaging measurements. The imaging data are being used to guide the development of a large-eddy simulation model of the recirculating bluff-body flow. Direct numerical simulation techniques to model turbulent jet and bluff-body flows, both nonreacting and reacting, are also being investigated. [5.0 FTE]

52. Chemical Kinetics and Dynamics

Tully, F.P.; Durant, J.L.; Chandler, D.W.; Miller, J.A.; Rohlfing, E.A.; Hayden, C.C.; Fisk, G.A.
Comm. 415-294-2316; FTS 234-2316

The goal of this research is to understand in detail the fundamental chemical processes that occur in combustion. Typical kinetics experiments use the laser-photolysis/laser-induced fluorescence technique to follow the course of reactions between, for example, OH and alcohols or between NH and oxidants. Recent experiments have discovered a catalytic mechanism for the dehydration of alcohols. A versatile flow-tube kinetics apparatus having both laser and mass-spectrometric diagnostics has been

completed. Recent theoretical studies have treated reactions such as those between H and NH₃, H and HNC, and F with CH₃OH using quantum-chemical and statistical-theoretical methods. Studies of dynamics emphasize collecting quantum-state-resolved data for elementary chemical processes. Photofragment-imaging studies of methyl-halide photodissociation and H + HI reaction have clarified the dynamics of these processes and the partitioning of excess energy. Recently initiated investigations of processes that occur on femtosecond time scales are providing insight about how energy moves throughout molecules. Studies of carbonaceous clusters produced by laser vaporization are a focus of research aimed at determining how soot precursors form during combustion. Theoretical and experimental investigations of C₃ clusters show that this species exhibits complicated dynamics on a potential-energy surface that has an unusually flat bend and strong stretch/bend interaction. [5.0 FTE]

Atomic Physics

Argonne National Laboratory Argonne, IL 60439

Physics Division \$1,532,000

- 53. Atomic Physics at ATLAS**
Dunford, R.W.; Berry, H.G.
Comm. 708-972-4052; FTS 972-4052

In this project, the physics of highly charged ions is studied using the Argonne Tandem/LINAC Accelerator System (ATLAS) heavy-ion accelerator. The electron cyclotron resonance (ECR) ion source, which is part of the uranium upgrade of ATLAS, is also used in these studies. The ECR ion source is on a high-voltage platform which allows the use of ion beams with energies up to 300 keV times the extracted ion charge state. Atomic physics research at ATLAS includes studies of atomic structure and ion-atom collisions. The atomic structure work aims at precision tests of quantum electrodynamics and relativistic quantum theory. The program features ultraviolet (uv) and X-ray spectroscopy and measurements of the lifetimes for forbidden decays in few-electron systems. The work on ion-atom collisions aims at understanding the dynamics of these collisions and has applications in fusion energy research, plasma physics, and astrophysics. A polarized sodium target is being used at the ECR ion source to study polarization transfer in ion-atom collisions. Another program is a high-resolution study of dielectronic recombination (DR) by channeled ions. The uranium upgrade of ATLAS makes possible the study of collisions between two very heavy nuclei at energies near the Coulomb barrier. [4.5 FTE]

- 54. Interactions of Fast Atomic and Molecular Ions with Solid and Gaseous Targets**
Kanter, E.P.
Comm. 708-972-4050; FTS 972-4050

Argonne National Laboratory's 4.5-MV Dynamitron accelerator is used to study the interactions of fast (MeV) atomic and molecular ions with matter. A unique feature

of the apparatus is the exceptionally high resolution ($\sim 0.005^\circ$ and ~ 200 psec) in angle and time-of-flight obtained in detecting particles emerging from the target. Unique multiparticle imaging detector systems have been developed which allow detection of multiparticle events consisting of up to 12 particles and yielding three-dimensional views of the particle trajectories. The work includes a general study of the interactions of fast charged particles with matter, emphasizing those aspects that take advantage of the unique features inherent in employing molecular-ion beams (e.g., the feature that each molecular ion forms a tight cluster of atomic ions that remain correlated in space and time as it penetrates the target). These techniques allow the direct determination of the geometrical structures of the individual molecular ions entering the target. These measurements have provided the first direct measurements of not only the spatial probability densities of the nuclei, but also their correlations in several small polyatomic molecules. Recent studies have probed the structure of H₂O⁺. [3.7 FTE]

- 55. Fast Ion-Beam/Laser Studies of Atomic and Molecular Structure**

Young, L.
Comm. 708-972-8878; FTS 972-8878

This program is directed toward the detailed understanding of atomic and molecular ion structure through high-resolution laser and radio-frequency studies in accelerated beams. The atomic structure measurements provide precision tests of quantum electrodynamics (QED) and relativistic quantum mechanics in few-electron systems, as well as experimental guides to the *ab initio* understanding of hyperfine structure in multielectron systems. The molecular structure measurements provide tests of *ab initio* computation of wave functions and molecular parameters of simple diatomic molecules for the first row of the periodic table, in addition to radio-frequency data of use to astronomers. A program to make precision oscillator-strength measurements (0.1%) on a few test case atomic species has been initiated. Finally, collaborative efforts are continuing with the medium-energy physics and weak interactions groups in the Argonne Physics Division to develop laser-driven polarized sources of hydrogen and techniques for trapping and polarizing gas-phase radioactive atoms. [2.5 FTE]

Brookhaven National Laboratory Upton, Long Island, NY 11973

Department of Applied Science \$225,000

- 56. Atomic Physics Research**
Johnson, B.M.
Comm. 516-345-4552; FTS 666-4552

Photoionization and related processes are studied using synchrotron radiation, gas-phase targets, ion beams, and ion traps. Most of the work utilizes the X-26 beamline at the National Synchrotron Light Source (NSLS). Noble-gas targets allow for the study of isolated, closed-shell atoms. Ion-source systems are developed to extend measurements to open-shell systems and to make systematic studies along isoionic, isoelectronic, isonuclear, and isoionic sequences. Very cold, multiply ionized atoms are

produced at energies of less than 100 meV through inner-shell photoionization in ion traps. Rate coefficients for charge exchange in symmetric and asymmetric interactions are measured at collision energies much lower than attainable by any other technique. Fluorescence radiation and electron emission following the primary photoionization event are monitored, and the final charge-state distributions, after accounting for charge exchange in subsequent ion-atom interactions, are measured. [2.3 FTE]

**Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720**

Chemical Sciences Division \$655,000

57. High-Energy Atomic Physics

Gould, H.A.

Comm. 415-486-7777; FTS 451-7777

The goals of this program are: to search for an electron electric dipole moment (EDM), to understand atomic collisions of relativistic ions, and to test quantum electrodynamics in a strong static Coulomb field. Recent results include a new upper limit to the electron EDM of 1×10^{-26} e cm, a factor of 7 improvement over all previous measurements and the smallest upper limit for any particle. Finding an electron EDM would be proof of new physics, not contained in the Standard Model, and would be as significant a discovery as the results expected from the Superconducting Super Collider. Present activities include: (1) increasing the sensitivity of the EDM experiment; (2) developing a new, nonchanneling technique for measuring electron impact ionization cross sections of highly stripped heavy ions; and (3) attempting to observe a new relativistic atomic collisions process, the capture of an electron by a (bare) ion, when the electron is produced as part of an electron-positron pair by the motional Coulomb fields of relativistic ion passing within atomic distances of a target nuclei. [2.5 FTE]

58. Atomic Physics

Prior, M.H.

Comm. 415-486-7838; FTS 451-7838

The structure and interactions of atomic systems are studied to provide the most detailed description of their behavior, and to stimulate theoretical understanding of the observed phenomena. The approach to this work emphasizes research topics that are best addressed with unique tools and expertise available at Lawrence Berkeley Laboratory (LBL). Currently the program exploits the ability of state-of-the-art electron cyclotron resonance (ECR) ion sources at LBL to produce intense, highly charged beams for the conduct of low-energy ion-atom collision studies. Current emphasis is upon multiple electron transfer phenomena and Auger electron spectroscopy. The program benefits substantially from collaborative efforts with colleagues from outside LBL. [1.2 FTE]

**Oak Ridge National Laboratory
Oak Ridge, TN 37831-6377**

Physics Division \$1,505,000

59. Theoretical Atomic Physics at Oak Ridge National Laboratory (ORNL)

Bottcher, C.

Comm. 615-574-4580; FTS 624-4580

The computational and mathematical techniques of modern theoretical physics are applied to interactions between atoms, ions, electrons, and photons over a wide range of energies, from a few electron volts to ultrarelativistic energies. Emphasis is on processes involving highly charged ions of interest in fusion plasmas, X-ray lasers, and accelerator-based atomic collision experiments. The techniques used include numerical lattice solutions of the time-dependent Schroedinger and Hartree-Fock equations by basis-spline collocation methods, coupled channel calculations, Monte Carlo evaluation of Feynman diagrams, and Born expansion and distorted wave techniques. A major new thrust is to convert several large codes to run on a massively parallel computer, with a view to performing realistic simulations of atomic and molecular processes in plasma and surface environments. Applications have been made to processes at nonrelativistic energies such as capture and ionization, in ion-atom collisions, and multiphoton ionization by intense laser beams. Recent studies include secondary electron spectra in proton-hydrogen and bare carbon-neon collisions at intermediate energies, and laser multiphoton ionization by circularly polarized light. Successful interpretations have been provided for recent experiments on cusp electrons and post-collision effects in ion-atom collisions. The program on relativistic collision physics is focused on phenomena important in accelerator and detector design (e.g., pair production with capture and free pair backgrounds in heavy-ion colliders). Detailed comparisons are made of perturbative and non-perturbative treatments of pair production. [1.0 FTE]

60. Accelerator Atomic Physics

Datz, S.; Dittner, P.F.; Krause, H.F.; Vane, C.R.

Comm. 615-574-4984; FTS 624-4984

The project objective is to achieve a detailed understanding of the interactions of high-energy, multiply charged ions with gas and solid targets, and with electrons. The facilities used for this research are the EN Tandem Accelerator and the beamlines on the Holifield Heavy Ion Research Facility (HHIRF). Experiments are being conducted to test whether the electrons contained in a crystal channel can be quantitatively treated as an almost free dense electron gas target. Using the HHIRF 25-MV tandem, beams of H-like, He-like, and Li-like calcium and titanium are produced and channeled at energies starting below, and proceeding through resonances for dielectronic excitation. The resulting X rays, from the decay of the dielectronically excited state, are measured in coincidence with ions that have captured an electron as a function of the ion energy. Since the cross sections are delta functions at the resonance energy, the energy width of the excitation function should reflect the Compton profile of the electrons in the channel. Radiative electron capture in crystal channels is being studied as a function of the ion energy loss and use of crystal models to determine impact parameter

dependent cross sections. At the European Center for Nuclear Radiation (CERN), 200 GeV/nucleon sulfur beams are being used to study lepton pair production cross sections as a function of angle, lepton energy, and target Z . The double excitation of helium by fast, bare ions is being measured as a function of the charge of the projectile. The variation of the cross section of different doubly excited states as a function of the projectile charge distinguishes the different excitation mechanisms. [4.6 FTE]

61. EN Tandem Operations

Dittner, P.F.

Comm. 615-574-4789; FTS 624-4789

The EN-Tandem Van de Graaff is operated for atomic physics research. A wide variety of light ions and multiply charged heavy ions are furnished by the EN Tandem at MeV energies for the accelerator atomic physics group, and for outside users from other divisions of Oak Ridge National Laboratory (ORNL), universities, and industry. Terminal voltages up to 6.5 MV are routinely available, and ion sources are sufficiently versatile to provide beams of all ions from protons through fluorine, silicon through chlorine, as well as beams of many heavier ions including nickel, iodine, gold, and uranium. A VAX-11/750/CAMAC-based data acquisition system, the Elbek magnetic spectrograph with position sensitive detectors, a high-resolution electron spectrometer, Si(Li) detectors, and a curved crystal spectrometer are available to users. Recent major beam usage has included inelasticity and impact parameter dependence studies of charge-correlated multiple ionization of neon and argon by carbon ions, double excitation of helium by fast bare ions, convoy electron studies, electron-electron interactions in transfer and excitation, angular distribution of Auger electrons following the collision of highly charged ions with a helium target gas, and the channeling of oxygen ions through thin crystals. [1.3 FTE]

62. Collisions of Low-Energy Multiply Charged Ions

Phaneuf, R.A.; Meyer, F.W.; Havener, C.C.

Comm. 615-574-4707; FTS 624-4707

Experimental studies of interactions of multicharged ions with neutral atoms are carried out at the lowest attainable kinetic energies, where the electronic potential energy of the reactants becomes an appreciable fraction of the available interaction energy and inelastic collision cross sections depend strongly on the potential-energy curves of the interacting system. Quantitative study of such processes yields important information about quasi-molecular structure and collision dynamics. Emphasis is currently on merged-beam measurements of absolute electron-capture cross sections and direct comparison of results with developing theoretical models at energies in the range from 0.1 to 1000 eV/amu, where the process is poorly characterized. Recent results for electron capture by multicharged oxygen ions from hydrogen atoms using an improved apparatus confirm the predicted increase in the cross sections at the lowest energies caused by capture into the 3 or 4p levels. Solid surfaces also provide a convenient reservoir of electrons for the study of atomic interactions, and exploratory experimental studies of the neutralization of multiply charged ions in grazing ion-surface interactions are in progress. The current emphasis is on characterizing the energy and angular

distributions of ejected electrons in order to better understand neutralization mechanisms. [1.0 FTE]

**Sandia National Laboratories, Albuquerque
Albuquerque, NM 87185**

Division of Lasers and Plasma Processing Sciences **\$130,000**

63. Atomic Processes in Reactive Plasmas

Greenberg, K.E.; Hargis, P.J.; Gerardo, J.B.

Comm. 505-844-1243; FTS 846-1243

The goal of this project is to gain an understanding of the fundamental electron/molecule and chemical mechanisms occurring in low-temperature glow discharges. These types of plasmas are commonly used to process materials, e.g., chemical vapor deposition of thin films and reactive ion etching. Various experimental methods including Raman spectroscopy, laser-induced fluorescence, optical-van spectroscopy, infrared absorption spectroscopy, and microwave interferometry are used to determine neutral and charged particle densities throughout the plasma. Optical and optical-microwave techniques are used to measure Stark shifts of atomic and/or molecular energy levels to determine electric field strengths in the sheath regions (and the bulk) of the plasma. Numerical simulations are also an important element of the research. These simulations, based on Boltzmann and hybrid Boltzmann-fluid codes, will be used to determine the electron-energy distribution function and to help understand the complex chemical mechanisms in these systems. Comparisons between experiment and simulation are the key to unraveling the physics and chemistry of these plasmas. [1.0 FTE]

Chemical Energy

**Ames Laboratory
Iowa State University
Ames, IA 50011**

Processes and Techniques Program **\$1,241,000**

64. Organometallic Complexes in Homogeneous Catalysis

Angelici, R.J.

Comm. 515-294-2603

The goal of this project is to understand how organosulfur compounds in petroleum feedstocks are desulfurized upon reaction with hydrogen gas over heterogeneous transition metal catalysts. This large-scale hydrodesulfurization (HDS) process involves initial adsorption of the organosulfur compounds at a metal site on the catalyst surface, followed by reactions that result in cleavage of the carbon-sulfur bonds to give H_2S and hydrocarbons. Since thiophenes are the most difficult compounds to desulfurize, current efforts focus on studies of thiophene binding

and reactions that might occur on catalyst active sites. It has been established that thiophene is able to coordinate to metal centers in a remarkable number of ways: (1) via the sulfur, (2) via two or four carbon atoms, or (3) via all five atoms of the ring. Each mode of coordination activates the thiophene to react in different ways. Coordination via either the four carbons or the entire thiophene ring leads upon reaction with hydrogen sources to the cleavage of both carbon-sulfur bonds and the complete desulfurization of thiophene. Two fundamentally different mechanisms for the HDS of thiophene have been proposed based on these studies. [2.0 FTE]

65. *Chemical Kinetics and Reactivity of Transition Metal Complexes*

Espenson, J.H.

Comm. 515-294-5730

The general goal of this project is to understand the homogeneous chemistry that underlies catalytic processes including synthetic fuels formation. Efforts are directed at reactions in homogeneous solution in which metal-carbon bonds are made and broken. One reaction of fundamental interest is the bond homolysis process $L_nM-R \rightarrow L_nM + R\cdot$, and its reverse, radical capture or colligation. The kinetics of thermally induced homolysis reactions are being examined for complexes of chromium, nickel, and cobalt; metal-carbon dissociation energies can be derived from such determinations. Very rapid colligation rates are being determined by means of laser flash photolysis experiments. Other reactions of metal alkyl complexes in which the metal-carbon bond is cleaved are also being studied, including bond hydrolysis and electrophilic reactions. Another aspect of this work concerns the kinetics and mechanisms of reactions in which alkyl radicals react with transition metal complexes. These include other colligation reactions, as well as reactions in which the free radical is oxidized or reduced by a transition metal. Reactions of $R\cdot$ with O_2 are also being studied. Electron transfer reactions of excited-state complexes are also under investigation for $Cr(\text{polypyridyl})_3^{3+}$ and $Cr(\text{cyclam})(NH_3)_2^{3+}$. [4.2 FTE]

66. *Multiple Pulse NMR Studies: Catalysis and the Chemical Constitution of Coal*

Gerstein, B.C.

Comm. 515-294-3375

Transient techniques in NMR of solids are used to probe the physics and chemistry of materials involved in heterogeneous catalysis, fossil fuels, and materials science. Examples include: (1) the use of multiple quantum spin counting of strongly dipolar coupled clusters of protons to determine stoichiometries of hydrocarbon fragments adsorbed on supported bimetallic catalysts used for reforming; (2) the use of NMR of quadrupolar nuclei such as ^{133}Cs and ^{63}Cu to characterize the chemical states of catalysts such as zeolites and alkali metal-doped copper oxides, and the use of NMR of ^{51}V and ^{17}O to characterize possible active sites for C_4 hydrocarbon oxidation in vanadium-phosphorus-oxide catalysts; (3) the use of dipolar oscillation NMR to determine internuclear distances in unstable organic molecules trapped in frozen matrices at 80 K; and (4) the use of variable-angle spinning to narrow the central transition of quadrupolar nuclei such as ^{17}O in active catalysts. [2.9 FTE]

67. *Fundamental Investigations of Supported Metal Catalysts*

King, T.S.

Comm. 515-294-9479

Most of the effort of this project is focused on elucidating the details of the fundamental catalytic phenomena made uniquely possible by highly dispersed, small metal particles. The general approach taken is to systematically vary catalyst composition, characterize in detail the surface of the resulting material, probe the chemisorption behavior of various molecules, and correlate this information with catalytic performance. The intent of this work is to probe the synergistic effects of adding a second element; the second element is either another metal to form a bimetallic or a catalyst poison or promoter. Specifically, the following phenomena are probed: (1) the role of ensemble size and electronic effects induced by addition of the second metal in a bimetallic system; (2) the influence of additives on metal crystallite morphology and the resulting modification of catalytic behavior; (3) the mechanism of promotion and poisoning; and (4) the nature of small hydrocarbon (and other) molecules chemisorbing and subsequently reacting on small metal and bimetallic particles. This work uses solid-state NMR (of 1H , ^{13}C , ^{63}Cu , and other nuclei) in combination with various traditional catalytic experiments and model reaction studies. [1.9 FTE]

68. *Spectroscopic and Kinetic Characterization of Metal Oxide and Sulfide Catalysts*

Schrader, G.L.

Comm. 515-294-0519

In this research, a fundamental understanding is being developed of metal oxide and sulfide catalysts, including the mechanisms of catalytic reactions, the structure and composition of catalysts, and the properties of surfaces. Metal oxides and sulfides are used extensively by industry for selective oxidation and hydrodesulfurization. Specific applications include paraffin oxidation and the hydroprocessing of organic sulfur compounds found in coal-derived liquids and petroleum. A complement of experimental approaches is used in this research involving kinetic measurements and comprehensive catalyst characterization. *In situ* spectroscopic techniques, such as laser Raman, Fourier transform infrared, and NMR spectroscopies are emphasized since they can be used to examine functioning catalysts at elevated temperatures and pressures. The goal of this research program is to provide fundamental relationships between catalyst structure, composition, and surface properties and the activity and selectivity of metal oxides and sulfides. [2.2 FTE]

69. *High-Temperature Gas-Phase Pyrolysis of Organic Compounds*

Trahanovsky, W.S.

Comm. 515-294-2886

The goal of this research is to understand in detail fundamental thermal reactions of organic compounds, especially those related to the pyrolysis of coal and coal-derived liquids. Work focuses on reactive molecules that are products of primary thermal reactions. The approach includes (1) developing new methods to prepare these molecules, (2) developing new spectroscopic techniques to characterize them, and (3) studying their reactions to characterize their chemistry. Reactions being studied

include their self reactions (oligomerization and polymerization), reaction with other species, and reactions in which they are transient intermediates. The work involves extensive use of flash vacuum pyrolysis, a convenient and effective technique for the study of the primary thermal reactions of organic compounds. Studies have concentrated on quinodimethanes, a large class of reactive molecules. A major objective of this work is to obtain a thorough understanding of the factors that affect the reactivity of *ortho*-quinodimethanes. Specific reactive molecules being studied include *ortho*-quinodimethanes derived from benzene, naphthalene, phenanthrene, furan, thiophene, and pyridine. A flow nuclear magnetic resonance (NMR) technique has been developed which allowed the ^1H NMR spectra of several very reactive *ortho*-quinodimethanes to be obtained for the first time. Other special techniques required to obtain the NMR spectra of reactive molecules are under development. In addition to studies involving model compounds, some studies involve the pyrolysis of coal itself. The objective of these studies is to identify by low-temperature ^1H and ^{13}C NMR spectroscopy the reactive molecules or types of reactive molecules produced by the pyrolysis of coal. [2.0 FTE]

Argonne National Laboratory Argonne, IL 60439

Chemical Technology Division \$600,000

70. Fluid Catalysis

Rathke, J.W.; Chen, M.J.; Klingler, R.J.
Comm. 708-972-4549; FTS 972-4549

This project uses an array of *in situ* high-pressure kinetic and spectroscopic techniques to determine reaction mechanisms and to explore new catalytic chemistry. Current research exploits the unique properties of supercritical fluids to uncover effects of extremely high diffusion rates on the catalytic reactions of gases, and to potentially alleviate gas-liquid mixing and catalyst-recovery problems typical of many homogeneous catalytic processes. Using *in situ* high-pressure ^{59}Co , ^{13}C , and ^1H NMR spectroscopies to determine steady-state and equilibrium concentrations of species present in the cobalt carbonyl catalyzed hydroformylation of propylene (Oxo catalysis) in supercritical carbon dioxide, improved yields of linear to branched products were demonstrated, and key features of the reaction mechanism were quantified. Carbon-hydrogen bond activation processes are also being explored to develop catalytic routes for the polymerization of small organometallic precursor molecules to yield preceramic polymers. Recently, a soluble electrophilic zirconium complex was found to efficiently catalyze the oligomerization of Al_2Me_6 . The organometallic chemistry of reactive metallophthalocyanine radicals with the aim of achieving solution-phase stereoselective functionalization of hydrocarbons is also under investigation. In research relevant to the activation of CH_4 , the first organic soluble hydride, methyl, and metal-metal bonded phthalocyanine complexes were prepared. [3.1 FTE]

Chemistry Division

\$1,950,000

71. Chemical Constitution of a Low-Volatile Bituminous Coal

Stock, L.M.

Comm. 708-972-3570; FTS 972-3570

Chemical and spectroscopic methods are being used to establish the constitution of Pocahontas No. 3 coal (Argonne Premium Coal Sample Program 5). This higher ranking coal was selected for study to investigate the general proposal that such highly aromatic coals have a lower degree of polymerization and, generally speaking, a simpler structure than low ranking subbituminous coals or lignites. Samarium(II) iodide was used for the removal of unpaired electron spin density from this coal. The CP and Bloch decay methods have been assessed for quantitative reliability, and tetrakis(trimethylsilyl)silane was used as a quantitative standard for ^{13}C nuclear magnetic resonance (NMR) spectroscopy. The results indicate that 90% of the carbon atoms are visible and their distribution among aliphatic and aromatic carbon atoms has been determined. These data are coupled with information on the Ru(VIII) oxidation products to elaborate the aliphatic carbon atom distribution. The new magnetic resonance data indicate biaryl linkages and imply that there are four to five rings per aromatic molecule. Base catalyzed reactions and base catalyzed C-alkylation are very promising for depolymerization and solubilization, respectively. [0.7 FTE]

72. Premium Coal Sample Program

Vorres, K.S.

Comm. 708-972-7374; FTS 972-7374

Eight U.S. coals have been collected, processed, and packaged to preserve the original properties of the pristine coals as much as possible. Over 530 orders have been filled of more than 14,000 ampoules. The material in the ampoules will meet the demand for another one to two years for the sample with the smallest inventory, and the reserves will continue to meet the current demand level for several decades. The gas atmosphere is monitored to establish sample stability. A users' handbook has been updated to include the most current bibliographic information, and a literature summary is being prepared by a group of experts. A symposium on "Research with Argonne Premium Coal Samples" was organized in conjunction with the fall 1990 American Chemical Society meeting. [0.5 FTE]

73. Characterization and Reactivity of Coals and Coal Macerals

Winans, R.E.; Hayatsu, R.; Dyrkacz, G.R.; Botto, R.E.; Carrado, K.A.; McBeth, R.L.; Melnicoff, P.E.; Bloomquist, C.A.A.

Comm. 708-972-7479; FTS 972-7479

The objective of this project is to obtain fundamental information on the chemical and physical structures of the Argonne premium coals and their maceral constituents to facilitate prediction of their thermal, chemical, and biological reactivity. Novel methods for the separation of coal macerals are being developed to provide ultrahigh-resolution partitioning of submaceral groups and to advance large-scale separation techniques. Argonne Premium Coal Samples and their separated macerals are subjected to selective modification and solubilization, and

to liquefaction (with Amoco Oil) to provide samples for a large array of characterization studies. Featured analytical approaches include true solid-state NMR imaging, laser desorption mass spectrometry, tandem mass spectrometry, and synchrotron X-ray absorption spectroscopy. Synthetic layered molecules with catalytic potential for large, coal-derived molecules are being designed, prepared, and characterized. Data about the premium coals are being assimilated into statistically accurate coal structures. This information is vital in the development of advanced processes for the utilization of fossil fuels. [9.0 FTE]

Brookhaven National Laboratory Upton, Long Island, NY 11973

Department of Applied Science \$700,000

74. High-Temperature Chemistry

Egan, J.J.

Comm. 516-282-4488; FTS 666-4488

This project addresses the thermodynamic, transport, and electronic properties of alloy and metal-molten-salt systems at high temperatures. Alloys are studied in both the liquid and solid state with emphasis on systems that form liquid and solid compound semiconductors. Both electrochemical and calorimetric measurements are being used to explore and characterize these systems. Galvanic cells using solid CaF_2 electrolytes are used to examine alloy systems and molten salts. Results yield metal activities, diffusion coefficients, ranges of homogeneity, as well as concentration and mobility of electrons and electron holes in alloy systems. In molten salts, the thermodynamic properties and conductivities are obtained. A high-temperature twin Calvet-type calorimeter is also operated to study ionic alloys. The electronic component of conductivity of molten salts is being examined by special polarization techniques, because this property is so important in determining the efficiency of electrolysis in the production of metals and the self-discharge of molten-salt batteries. Results of this work are explained in terms of atomic models. [3.2 FTE]

75. Metal Hydrides

Reilly, J.J.; Johnson, J.R.

Comm. 516-282-4502; FTS 666-4502

Knowledge of the behavior and properties of hydrogen/metal systems is essential for the successful implementation of many energy-related processes and applications. The prime concern of this program is to increase that store of knowledge through the determination of the thermodynamic, kinetic, and structural parameters of metallic hydrogen systems. A particular goal is to relate all pertinent data and hypotheses to develop a predictive capability regarding the behavior of a given system. This capability permits the synthesis of compounds having optimum properties for particular applications. Current topics of interest are reaction kinetics, properties of metal hydride suspensions, the preparation and characterization of a new class of hydrogen bronzes prepared from complex oxides, and the catalytic properties of metal hydrides. The major experimental tools and/or techniques are equilibrium pressure/temperature/composition measurements, X-ray diffraction, Fourier transform infrared

spectrometer (FT-IR) measurements, and the use of a high-pressure apparatus to study the kinetic behavior of metal hydride suspensions. [3.1 FTE]

Chemistry Department

\$1,532,000

76. Structure and Reactivity in Catalysis and Advanced Materials

Koetzle, T.F.; McMullan, R.K.; Andrews, M.;

Bullock, R.M.; Hrbek, J.

Comm. 516-282-4384; FTS 666-4384

Research efforts under this project are concerned with fundamental aspects of chemical catalysis, both homogeneous and heterogeneous, augmented by investigations of selected advanced materials. Many of the studies make use of the special facilities at Brookhaven National Laboratory (BNL), the National Synchrotron Light Source (NSLS) and the High Flux Beam Reactor (HFBR), often in collaboration with scientists from other institutions. Transition metal hydride complexes, ubiquitous key intermediates in homogeneous catalysis, constitute one primary focal point for the experimental work. Accurate structural data for these compounds, uniquely provided by neutron diffraction studies at the HFBR, are correlated with reaction mechanism investigations to elucidate an understanding of important metal hydride reactivity patterns. A particular emphasis concerns the factors that determine the rate and mode of M-H bond cleavage, e.g., homolytic ($\text{M} \cdot + \text{H} \cdot$) or heterolytic ($\text{M}^- + \text{H}^+$ or $\text{M}^+ + \text{H}^-$). These findings in turn support research, both at BNL and elsewhere, seeking ways to apply homogeneous catalysis to energy conversion and conservation. For example, the interactions of metal complexes with carbohydrates are being explored in order to develop a body of knowledge suitable for evaluating possible new chemical approaches to biomass conversion. Heterogeneous catalysis studies correlate structural investigations at the NSLS of adsorbates on metal surfaces, with corresponding catalytic reactions examined by traditional high-vacuum surface science and infrared spectroscopy techniques. A major objective of this work is the understanding of the molecular basis for the effects of catalyst promoters and poisons. Collaborative structural studies of advanced materials, utilizing both the HFBR and the NSLS, investigate high- T_c superconductors, fast-ion conductors, and gas clathrate hydrates. Results of these studies provide a foundation for both understanding and improving the special characteristics of these materials. [9.8 FTE]

Lawrence Berkeley Laboratory University of California Berkeley, CA 94720

Applied Science Division

\$100,000

77. Organometallic Models of the HDN Reaction: Bonding and Selective Hydrogenation of Heteroaromatic Nitrogen Compounds

Fish, R.H.

Comm. 415-486-4850; FTS 451-4850

Mono- and polynuclear heteroaromatic nitrogen compounds, an important class of model coal compounds, are

the focus of fundamental studies with homogeneous organorhodium and ruthenium metal complexes. Since this class of model coal compounds is directly involved in the hydrodenitrogenation (HDN) process, it is important that these fundamental studies include the mode of bonding of the nitrogen compounds to the metal centers, i.e., N- versus π -bonding, and the utilization of organorhodium and ruthenium complexes as catalyst precursors for the regioselective nitrogen heterocyclic ring hydrogenation reaction, the first step in the HDN process of nitrogen atom removal. Recently reported results with a (η^5 -pentamethylcyclopentadienyl)rhodium dication complex, $[\text{Cp}^*\text{Rh}(\text{CH}_3\text{CN})_3]^{2+}$, and several heteroaromatic nitrogen compounds, such as 2-methylpyridine (N); 2,4-dimethylpyridine (N); 2,4,6-trimethylpyridine (π); quinoline (N); isoquinoline (N); 1,2,3,4-tetrahydroquinoline (π); 2-methylquinoline (N), N-methylindole (π); N-methylpyrrole (π); acridine (N); phenathridine (N); 5,6- and 7,8-benzoquinolines (N) clearly indicated that N- versus π -bonding to the metal center depends on the structure of the nitrogen ligand and the availability of lone pair electrons on the nitrogen atom. It was found that Cp^*Rh complexes with the specific formula $[\text{Cp}^*\text{Rh}(\eta^1, \text{N-ligand})(\text{CH}_3\text{CN})_2]^{2+}$ were catalyst precursors in the regioselective hydrogenation of the nitrogen ring and this result clearly defines the role of initial N-bonding to the rhodium center and two replaceable CH_3CN ligands as critical for selective nitrogen ring reduction to occur. Further studies helped define relative rates as a function of ligand structure and nitrogen ligands that inhibited and enhanced the initial rate of nitrogen ring reduction. The mechanism of this selective hydrogenation was also studied with deuterium gas experiments and a high-pressure nuclear magnetic resonance spectroscopy technique using $[\text{Cp}^*\text{Rh}(\eta^1, \text{N-quinoline})(\text{CH}_3\text{CN})_2]^{2+}$ and $[\text{Cp}^*\text{Rh}(\eta^1, \text{N-2-methylpyridine})(\text{CH}_3\text{CN})_2]^{2+}$ as the catalyst precursors which provided information on reversible hydrogenation of the 1,2-N=C double bond and stereoselectivity in the reduction of the other C=C double bonds as well as intermediate hydride formation. Similar bonding studies with (η^5 -cyclopentadienyl)ruthenium cation (CpRu^+) and (η^5 -pentamethylcyclopentadienyl)ruthenium cation (Cp^*Ru^+) with a number of the heteroaromatic nitrogen ligands revealed that N- and π -bonding to the metal center for these ligands also depends on steric and electronic effects, but that these organorhodium complexes were not efficient catalysts for the selective hydrogenation reaction. [1.5 FTE]

Chemical Sciences Division \$1,070,000

78. High-Energy Oxidizers and Delocalized-Electron Solids

Bartlett, N.

Comm. 415-642-7259

The aim of this project is the synthesis and characterization of new materials that may have utility in efficient storage or usage of energy. The novel materials include two-dimensional networks of light π -bonding atoms (boron, carbon, and nitrogen) with structures akin to graphite. Of these the more metallic have possible applications as electrode materials for high-energy-density batteries, and those that are semiconducting could be useful in converting light to electrical energy. Good ionic conductors are also being sought, with emphasis on

lithium-ion and fluoride-ion conductors, since batteries based on lithium and fluorine would be unsurpassed in their energy-density features. In addition, novel oxidation-state fluorides are being synthesized and structurally characterized to provide a comprehensive basis for better theoretical models, which should bring an improved capability to predict physical and chemical behavior. Previously unknown or little studied high-oxidation-state species constitute a large part of this effort. Such species are also investigated for their efficiency and specificity as chemical reagents. [2.0 FTE]

79. Catalytic Hydrogenation of Carbon Monoxide

Bell, A.T.

Comm. 415-486-7095; FTS 451-7095

The purpose of this program is to develop an understanding of the fundamental processes involved in catalytic conversion of carbon monoxide and hydrogen to gaseous and liquid fuels. Attention is focused on defining the factors that limit catalyst activity, selectivity, and resistance to poisoning, and the relationship between catalyst composition/structure and performance. To meet these objectives, a variety of surface diagnostic techniques are used to characterize supported and unsupported catalysts before, during, and after reaction. The information thus obtained is combined with detailed studies of reaction kinetics to elucidate reaction mechanisms and the influence of modifications in catalyst composition and/or structure on the elementary reactions involved in carbon monoxide hydrogenation. [3.2 FTE]

80. Transition Metal Catalyzed Conversion of CO, NO, H₂, and Organic Molecules to Fuels and Petrochemicals

Bergman, R.G.

Comm. 415-642-2156

The goal of this project is the development of new chemical reactions in which transition metals interact with organic materials, and the understanding of how these reactions work and can be applied to the development of new potentially useful chemical transformations. Several years ago a major discovery on this project was that of the first alkane/transition metal C-H oxidative addition reactions (C-H activation). Two of the most significant recent discoveries in the project are that liquified xenon and krypton can be used as inert solvents for C-H activation, and that weak metal-alkane and metal-xenon (krypton) complexes intervene as intermediates in these reactions. Current work is directed toward utilizing these results (1) to activate a range of new substrates, such as solids and gases that are difficult to liquefy (e.g., methane); (2) to develop methods for determining the structure and investigating the reactivity of the transient alkane and noble gas complex intermediates involved in C-H insertion processes; (3) to understand the thermodynamics and kinetics of C-H activation; (4) to extend the process to O-H, N-H, and C-F activation; and (5) to develop better methods for using C-H activation to convert alkanes into functionalized organic compounds. [4.5 FTE]

81. Formation of Oxyacids of Sulfur from SO₂
Connick, R.E.
Comm. 415-642-4981; FTS 458-4981

Stimulus for the research is the existence of acid rain. Coal-burning power plants produce sulfur dioxide, which is oxidized in air to form sulfuric acid, the principal component of acid rain. In most commercial flue-gas desulfurization processes the sulfur dioxide is absorbed in an aqueous solution of low acidity where it may be oxidized by O₂. Control of the rate of this latter reaction is of major importance to these processes. While recent research has been concentrated on this reaction, investigation of the fundamental chemistry of species formed from sulfur dioxide and reactions of these species remains the primary goal. The oxidation-reduction chemistry of sulfur should be studied, particularly reactions between two oxidation states of the element (e.g., reactions involving HSO₃⁻, H₂S, S₈, and the polythionates). A secondary and not closely related goal is to determine the factors controlling the rate of substitution reactions in the first coordination sphere of metal ions in solution. Computer modeling has been extended to three dimensions, and configurations of activated complexes have been determined. The usual concept of a transition state with reflection coefficient near unity is quite inadequate. [1.0 FTE]

82. Potentially Catalytic and Conducting Polyorganometallics
Vollhardt, K.P.C.
Comm. 415-642-0286

This project involves the synthesis and evaluation of new, multimetallic molecules, designed to exhibit novel chemical behavior, particularly (1) the catalysis of organic transformations of synthetic and industrial importance and (2) potential conductivity. It centers on the development and execution of synthetic methodology aimed at allowing access to sequences of extended strong π -ligands to multiple transition metals. Although new work has as its target a variety of novel organic systems, most investigations so far have focused on the exploitation of a new, iterative strategy that allows the continued elaboration of linked cyclopentadienyl chains and their complexation with control of the resulting oligometallic sequence. A number of unknown transition-metal arrays have become available in which the metallic centers adopt "unnatural" linear and angular configurations. These structures give rise to unprecedented reactivity when exposed to small molecules, pointing toward applications in catalysis. They also provide ideal models with which to probe the elementary steps of multimetallic ligand and electron transfer. The discovery of exciting preliminary chemistry of these systems includes thermally and photochemically induced intramolecular transfer of organic fragments. Current efforts concentrate on exploring the reactivity patterns of the structures and expanding the range of available ligand chains. [2.6 FTE]

Los Alamos National Laboratory
University of California
Los Alamos, NM 87545

Isotope and Nuclear Chemistry **\$380,000**
Division

83. Transition Metal Mediated Reactions of SO₂
Kubas, G.J.; Burns, C.J.
Comm. 505-667-5846; FTS 843-5846

This research has focused on the basic chemistry of environmentally and energy-related small molecules, primarily SO₂ and H₂, mediated by transition metal complexes. A fundamental understanding of the cleavage of S=O and H-H bonds will allow insights into new methods of chemical conversion. Initial SO₂ binding followed by a wide variety of reactivity has been found to occur at both metal and ligand sites of organometallic complexes. Cp'₂V (Cp' = C₅Me₅) and SO₂ formed Cp'₂V(η^2 -SO₂) and then inserted a second SO₂ to give an unusual oxygen-bound chelating dithionite, Cp'₂V(η^2 -S₂O₄). Significantly, SO₂ has been found to undergo oxygen transfer reactions on several organometallic complexes in which SO₂ is effectively disproportionated to sulfur and SO₃. Sulfide-ligand based activation occurred on Cp'₂Mo₂(μ -S)₂(μ -S₂) and Cp'₂Cr₂(μ -S)(μ - η^2 -S₂)(μ - η^1 -S₂) to generate S₈ and thio-sulfate complexes such as Cp'₂M₂(μ -S₂)(μ -S)(μ -SSO₃) which trap the SO₃. Crystallography showed that SO₂ underwent bifunctional Lewis acid-base activation, initially coordinating via sulfur to the μ - η^1 -S₂ ligand of the Cr complex and in turn having its oxygens coordinated by "lattice" SO₂ molecules. The latter presumably then transfer oxygen to the sulfide-bound SO₂ to give SO₃. The SSO₃ ligand in Cp'₂Mo₂(S₂)(S)(SSO₃) can be reduced with H₂ to regenerate the starting complex, thus giving a catalytic cycle for SO₂ reduction to S₈ and H₂O. This discovery of side-on bonding of H₂ molecules to metals represents the first stable sigma-bond complex and serves as a prototype for other such activations, e.g., C-H in hydrocarbons. Studies of these complexes are providing an extremely detailed picture of bond rupture on a metal center. The first chromium-dihydrogen complex, Cr(CO)₃(PCy₃)₂(H₂), has recently been isolated as a solid which completely dissociates H₂ on dissolution to give Cr(CO)₃(PR₃)₂. The latter has an agostic C-H interaction isostructural with the W analogue. Activation of O-H bonds in H₂O on the same complexes that bind H₂ is also being investigated and the structure of W(CO)₃(P-*i*-Pr)₂(H₂O) shows the longest M-O bond, 2.32 Å, of any organometallic aquo complex. [1.4 FTE]

Oak Ridge National Laboratory
Oak Ridge, TN 37831-6268

Chemical Technology Division **\$566,000**

84. Kinetics of Enzyme-Catalyzed Processes
Greenbaum, E.; Woodward, J.
Comm. 615-574-6835; FTS 624-6835

A novel photophysical phenomenon was observed in isolated spinach chloroplasts that were metallized by precipitating colloidal platinum onto the surfaces of the

thylakoid membranes. A two-point irradiation and detection system was constructed in which a helium-neon laser was used to irradiate the platinized chloroplasts at varying perpendicular distances from a single linear platinum electrode in pressure contact with the platinized chloroplasts. No external voltage bias was applied to the system. The key objective of the experiment was to measure the relative photoconductivity of the chloroplast-metal composite matrix. Unlike conventional photosynthetic electrochemical cells where irradiated chloroplasts are in close proximity to an electrode or linked to the electrode by an electrode-active mediator, in the present experiments the flow of photocurrent was through the biocomposite material. A sustained steady-state vectorial flow of current in the plane of the entrapped composite from the point of laser irradiation to the wire electrode was measured. The absolute value of the measured photocurrent and the maximum perpendicular distance between the point of irradiation and the linear electrode for which sustained current could be measured depended critically on the experimental procedure used to prepare the platinized chloroplasts. The effect of guanidine hydrochloride on the hydrolytic activity and tryptophan fluorescence of the major cellulase component, cellobiohydrolase I, has also been studied. [4.0 FTE]

Chemistry Division

\$2,729,000

85. *Organic Chemistry and the Chemistry of Fossil Fuels*

Buchanan, A.C.; Britt, P.F.; Haganan, E.W.
Comm. 615-576-2168; FTS 626-2168

The objective is to conduct fundamental investigations that provide new insights into the chemical structure and reactivity of coal. Model systems are being developed to explore the impact of restricted diffusion on reaction mechanisms relevant to the thermal reactivity of coal. Current research focuses on: (1) thermolysis pathways for surface-attached phenethyl phenyl ether [$\approx\text{PhCH}_2\text{CH}_2\text{OPh}$] as a model for ether bridges prevalent in low-rank coals and lignites; (2) thermolysis of surface-attached 1,3-diphenylpropane [$\approx\text{Ph}(\text{CH}_2)_3\text{Ph}$] and 1,4-diphenylbutane [$\approx\text{Ph}(\text{CH}_2)_4\text{Ph}$] as models for cross-linked structures in the macromolecular network of coal; and (3) the role of solid-state interactions in acid-catalyzed cracking of $\approx\text{Ph}(\text{CH}_2)_3\text{Ph}$ with aluminosilicates in dispersed solids. Solid-state nuclear magnetic resonance (NMR) techniques such as double cross polarization (DCP) and rotational echo double resonance (REDOR) are being developed for studies of the structure of chemically modified coals. Research focused on ^1H - ^{19}F - ^{13}C DCP/MAS ^{13}C -NMR when coupled with selective chemical derivatization of coal with fluorine, reveals localized structure information on carbon centers in the vicinity (ca. 4 Å) of fluorine atoms. The chemistries of several selective fluorinating agents, such as *N*-fluoro-*N*-alkyl-*p*-toluenesulfonamides, are being developed for application to coal. Derived information will contribute to the base of scientific knowledge necessary for the development of novel concepts for the conversion of coal to chemicals or fuels in an economically viable, environmentally acceptable manner. [4.6 FTE]

86. *Basic Aqueous Chemistry to High Temperatures and Pressures*

Mesmer, R.E.; Holmes, H.F.; Palmer, D.A.; Simonson, J.M.; Ho, P.C.
Comm. 615-574-4958; FTS 624-4958

The aim of this program is to establish basic principles governing chemical and thermodynamic behavior of aqueous solutions of broad classes of solutes at high temperatures and pressures. Advancement in experimental methods and the development of new models for exploring and representing behavior over wide extremes of conditions are important parts of this program. A range of diverse but complementary techniques are employed to obtain precise data to and beyond the critical conditions of water and its solutions. Chemical processes under present study are ionization-ion association, complexation, hydrolysis, solubilities, volatilities, and oxidation reduction. Thermodynamic quantities of interest are excess properties and ion-interaction parameters, molar volumes, and reaction thermodynamics. Principal methods in use are: flow calorimetry, isopiestic methods, electrochemical cells, electrical conductivity, densimetry, liquid-vapor partitioning, and Raman spectroscopy. New results are leading to models for describing variations with temperature, pressure, and composition for both standard state and excess thermodynamic quantities. A new initiative is being explored to represent solution properties using molecular dynamics simulations. Results for this program have major impact in basic solution chemistry, basic hydrothermal geochemistry, steam generation technology, utilization of geothermal resources, nuclear waste disposal, and environmental transport of metals. The approaches and techniques developed here for species identification and the study of reaction equilibria have broad applicability in the waste management and environmental restoration activities of the Department of Energy. [4.1 FTE]

87. *Heterogeneous Catalysis Related to Energy Systems*

Overbury, S.H.; Huntley, D.R.; Mullins, D.R.; Krause, M.O.
Comm. 615-574-5040; FTS 624-5040

Surface structure and reactivity are determined on single crystal metals, with particular emphasis on model hydrodesulfurization and bimetallic systems. Adsorption and reactions of methanethiol, benzenethiol, hydrogen sulfide, mercaptoethanol, thiophene, and tetrahydrothiophene have been studied on Ni(110), Ru(0001), and W(001). Reaction products are monitored by temperature programmed desorption techniques, while the identity and orientation of molecular species on the surface are determined as a function of coverage and temperature using spectroscopic methods including near edge X-ray absorption fine structure, high resolution electron energy loss, and X-ray and ultraviolet photoelectron spectroscopies. Recently, attention has been focused on reactions of polyfunctional adsorbates and between coadsorbed species on Ni(110). Angle dependent ion scattering has been used to determine the structure and growth of metal overlayers including Cu/Ru(0001), Ni and Cu on W, Sn on Pt(111) and Ni(111), and the surface structures of metal alloys (NiAl and Pt₃Sn). A recent initiative is to study the reactions of organosulfur molecules with the Ni/W system. Also, atomic spectroscopy and dynamics of excitation and

relaxation of free atomic species are examined using synchrotron radiation. Open shell atoms such as O, Mg, Cd, Be, Ga, and the halogens are of particular interest. [4.0 FTE]

88. Photolytic Transformations of Hazardous Organics in Multiphase Media

Zingg, S.P.; Sigman, M.E.; Pagni, R.M.

Comm. 615-576-7325; FTS 626-7325

This program investigates the photochemistry of aromatic hydrocarbons (ArH) and polynuclear aromatic hydrocarbons (PAHs) both in heterogeneous and aqueous media by product analysis and *in situ* spectroscopic techniques. The photochemistry of anthracene adsorbed on silica in heterogeneous organic slurries is being explored. In the presence of oxygen, anthracene undergoes rapid photodecomposition, while in the absence of oxygen very little photoreaction is observed. This behavior stands in stark contrast to the photoreactivity of anthracene in homogeneous organic solutions. The photochemistry of ArHs and PAHs in aqueous media, though of significant environmental concern, has not been well studied. The photolysis of anthracene in water has also been examined, and the product distribution varies significantly as a function of the oxygen concentration. In oxygen-deficient aqueous solution, the formation of an unreported product from the primary photodecomposition pathway of anthracene has been observed. The formation of this new product is consistent with the involvement of a previously postulated cation radical pathway in the aqueous photooxidation of PAHs. These studies will be of value in enhancing the basic understanding of photochemical processes occurring at interfaces and under environmentally relevant conditions. [2.4 FTE]

**Pacific Northwest Laboratory
Richland, WA 99352**

Chemical Sciences Department \$655,000

89. Free-Radical Chemistry of Coal

Franz, J.A.; Alhajjar, M.S.; Autrey, S.T.; Linehan, J.C.

Comm. 509-375-2967

The objective of this project is to determine kinetics and mechanisms of key radical and radical ionic pathways important to thermal degradation of coal. Efforts include determination of bond strengths of C-H, S-H, and C-S bonds; absolute rates of organic free-radical rearrangements; and rate expressions for atom transfer reactions involving radicals and radical ions. Methods include nanosecond kinetic laser flash photolysis, kinetic electron paramagnetic resonance spectroscopy, and laser photoacoustic calorimetry. Homolytic cleavage of carbon-sulfur and carbon-selenium bonds in reactions with carbon, phosphorus, and metal-centered radicals are under investigation. *Ab initio* quantum chemical calculations at various levels of electron correlation are being investigated to examine excited state and open shell potential surfaces of organosulfur intermediates and radical rearrangements. A theoretical and experimental study of the radical hydrogen transfer mechanism for the cleavage of aryl-alkyl bonds is under way. Solid-state NMR methods for the characterization of organosulfur structure in coal

using ^{15}N and ^{195}Pt detection are under development. [3.7 FTE]

**Solar Energy Research Institute
Golden, CO 80401**

**Fuels and Chemicals Research \$400,000
and Engineering Division**

90. Basic Research in Synthesis and Catalysis

DuBois, D.L.; Curtis, C.J.

Comm. 303-231-7371; FTS 327-7371

The project objective is the synthesis of new catalysts for the electrochemical reduction of CO_2 and CO to methanol. A new class of CO_2 reduction catalysts has been discovered that is based on palladium triphosphine complexes. These complexes catalyze the electrochemical reduction of CO_2 to CO. Kinetic and mechanistic studies of this reaction have been completed. This information is currently being used to design more stable and more selective catalysts. Efforts are also under way to prepare other CO_2 reduction catalysts. Similar studies are in progress to develop homogeneous catalysts for the electrochemical reduction of CO. In this effort two important steps have been demonstrated. First, the reaction of late transition metal hydrides with electrophilic carbonyl complexes to produce metal formyl complexes has been demonstrated and shown to have some generality. Second, it has been demonstrated that some of these hydrides can be generated by electrochemical reduction. Current efforts are directed at developing a catalytic cycle based on this chemistry and understanding these fundamental reactions. [2.6 FTE]

Separations and Analysis

**Ames Laboratory
Iowa State University
Ames, IA 50011**

Processes and Techniques Program \$1,103,000

91. Analytical Separations and Chemical Analysis

Fritz, J.S.

Comm. 515-294-5987

The project objective is to devise practical, innovative methods for separation and chemical analysis. Chromatographic separation and speciation of anions and metal cations are accomplished by ion chromatography and by complexation (of metal ions), followed by liquid chromatographic separation. New resins and complexing reagents are synthesized as part of this research. Resins with hydrophilic chemical substituents are highly effective for use in solid-phase extraction. Chelating reagents and resins are prepared and used for isolation of selected metal ions from aqueous samples. These new materials will be useful in attacking the waste cleanup problems of the 1990s. New liquid-chromatographic and gas-chromatographic

methods are being developed for the important problem of determining small amounts of water in chemicals and other materials. [2.1 FTE]

92. Analytical Spectroscopy

Houk, R.S.; D'Silva, A.P.
Comm. 515-294-9317

The project objective is the development of new techniques for ultratrace analysis. Excitation sources for atomic spectroscopy, such as inductively coupled plasmas (ICPs), inert gas afterglows, and laser-produced microplasmas, are studied by both optical and mass spectroscopy. Typical studies include characterization of the noise behavior of ICPs, investigation of the extraction process and interferences in ICP mass spectrometry, and elucidation of energy transfer processes in ICPs and afterglows. These atomic excitation sources are coupled with chromatographic separations to provide element-selective detection for elemental speciation. New methods for ion trapping and time-of-flight mass spectrometry are also investigated. [4.21 FTE]

93. Chemical Analysis at Liquid-Solid Interfaces

Porter, M.D.
Comm. 515-294-6433

This project examines new approaches for the construction and characterization of monomolecular films at liquid-solid interfaces. Efforts focus on (1) developing atomic-scale descriptions of the two-dimensional arrangement of spontaneously adsorbed monolayer films formed from n-alkanethiols at gold and silver surfaces, (2) probing solvent-monolayer interactions of n-alkanethiol monolayers with aqueous and various nonaqueous solvents with *in situ* Fourier transform infrared reflection spectroscopy, and (3) examining the fabrication for molecular recognition monolayers with organosulfur derivatized cyclodextrin monolayers. The atomic-scale arrangements are probed by both scanning tunneling and atomic force microscopy. The molecular level descriptions are derived primarily from infrared reflection spectroscopy, optical ellipsometry, electrochemistry, and contact angle studies that relate the composition and molecular arrangement (spatial orientation and packing density) of the organic surface structures with the crystallinity and roughness of the substrate. The molecular recognition effort also examines the incorporation of size selective channels in long alkyl chain monolayers. [2.2 FTE]

94. Lasers in Analytical Chemistry

Yeung, E.S.
Comm. 515-294-8062

The central theme of this project is the identification, evaluation, and application of analytical concepts based on the most recent developments in spectroscopy, particularly laser technology. Solutions to a large number of chemical problems, especially those in environmental, clinical, and energy-related areas, are currently limited by available analytical methodology. Attempts will be made to remove limitations by developing new techniques for measurements, by providing novel instrumentation, and by gaining an in-depth understanding of the fundamental physical and chemical principles behind the measurements. Specific studies include (1) spatial and temporal spectroscopic probes to study laser vaporization and laser

desorption processes, so that quantitation can become more reliable; (2) electro-rotation and magneto-rotation techniques for selective measurements in solutions; (3) detectors for liquid chromatography and for thin-layer chromatography that are more sensitive and more reliable; and (4) laser-initiated gas-phase reactions relevant to vapor deposition and etching schemes for material processing. [4.1 FTE]

**Argonne National Laboratory
Argonne, IL 60439**

Chemistry Division

\$1,274,000

95. Separations Science Related to Nuclear and Hydrometallurgical Technology

Horwitz, E.P.
Comm. 708-972-3653; FTS 972-3653

The primary objectives of this project are: (1) to design, synthesize, and characterize new classes of aqueous-soluble complexing agents for metal ion separation. These new complexants are designed to form water-soluble, stable complexes with tri-, tetra-, and hexavalent metal ions in highly acidic media and to decompose under mild thermal and/or oxidizing conditions to form less environmentally noxious species; (2) to study extractant-diluent interactions with the objective of improving the solubility of highly polar extractants in hydrocarbons and understanding the basic similarities and differences in bulk phase extraction and extraction chromatography; and (3) to develop improved methods for synthesizing new and existing organophosphorus extractants and particularly extractants containing steric hindrance, by studying the pathways for converting one or more phosphorus-oxygen bonds into phosphorus-carbon or phosphorus-hydrogen bonds. All three objectives are directed toward applications in (1) nuclear technology, such as actinide separations, waste processing, and by-product recovery from nuclear waste and (2) hydrometallurgical processing and groundwater decontamination. [3.7 FTE]

96. Particle-Induced Desorption/Ionization Mass Spectrometry

Hunt, J.E.
Comm. 708-972-3517; FTS 972-3517

The particle-induced desorption mass spectrometry program is focused on the study of processes that occur in the emission of charged and neutral species as a result of particle and photon impact. Time-of-flight mass spectroscopy is used to study the interaction of fast ion and laser beams with organic surfaces. The goal of these studies is to elucidate the processes that occur, and thus provide new knowledge relevant to a broad base of analytical desorption mass spectrometric techniques. A comprehensive understanding of the interaction of fast particles with materials is sought since these interactions represent the first and most fundamental step in the desorption process. Areas of current interest include (1) MeV ion beam desorption of valine and (2) laser desorption and laser photoionization studies. The first study has revealed information on the effect of ion beam energy on the kinetic energy and emission angle of secondary ions. Complementary measurements on both ions and neutral molecules

are made using laser desorption/postionization techniques. [1.0 FTE]

**Brookhaven National Laboratory
Upton, Long Island, NY 11973**

Department of Applied Science \$497,000

97. Analytical Techniques with Synchrotron Radiation and Ion Beams

Jones, K.W.; Gordon, B.M.
Comm. 516-282-4588; FTS 666-4588

The project uses X-ray and ion-beam microscopy methods for study of catalysts, characterization of coal, and other chemical systems. Experiments to improve the performance of the synchrotron-based X-ray microscope are aimed at achieving a spatial resolution of 1 μm with a photon flux integrated over all energies of 10^{10} photons/(s- μm^2) or more. A number of different catalyst systems are being investigated with the X-ray microscope including polyolefins, fluid catalytic cracking (FCC) catalysts, and hydrotreating catalysts. Applications to studies of porosity and fluid flow in different systems, including catalysts, are being initiated. These experiments demand the highest possible values of X-ray microscope resolution and beam intensity. Ion beams are being used in complementary experiments to profile hydrogen and other light elements in several types of catalysts. [2.7 FTE]

98. Microparticle Analysis by Laser Spectroscopy

Tang, I.N.; Fung, K.H.
Comm. 516-282-4517; FTS 666-4517

The project focuses on building a fundamental understanding and exploring new applications of novel laser-based spectroscopic methods for chemical analysis of microparticles. Suspensions of micron-sized particles are abundant in nature, and in numerous energy-related processes as well. In order to elucidate the formation mechanisms and understand the subsequent chemical transformation under a variety of reaction conditions, it is imperative to develop analytical measurement techniques for *in situ* monitoring of these suspended particles. Such a task has always been a formidable one, since the mass of an individual particle is only on the order of nanograms and the composition is often complex. Current research interests include (1) elucidation of the transient states that result in Raman intensity enhancement by resonance absorption, (2) systematic investigation of the Raman scattering cross sections for ionic solids containing oxyanions, using a microparticle levitation technique, and (3) studies of other potentially important nonlinear optical processes such as stimulated emission and multiphoton absorption in droplets. Combined with state-of-the-art instrumentation the research will lead to increased sensitivity and better selectivity of spectroscopic methods for microparticle analysis. [1.9 FTE]

**Idaho National Engineering Laboratory
Idaho Falls, ID 83415-3527**

\$290,000

99. Negative Ionization Mass Spectrometry

Delmore, J.E.; Appelhans, A.D.; Dahl, D.A.
Comm. 208-526-2820; FTS 583-2820

Gas/solid negative ion formation processes are being studied to elucidate the ion formation/decomposition pathways. Examples are the formation of sulfur hexafluoride anions by electron capture and the subsequent decomposition back to the neutral molecule, and the formation of hydride ions when electrons impact on metal surfaces exposed to hydrogen. Current activity is centered on the study of ceramic ion sources that emit gas phase metal oxide anions upon heating. A type of ceramic now being studied emits substantial currents of the perhenate anion at temperatures of 900 to 1000°C. This is a new class of ion emitting material developed by this program which holds much promise for a variety of applications for probing surfaces for analysis. These materials are being studied by a combination of techniques including direct imaging of the ions as emitted from the source, mass analyzing the ions during operation, and post analyzing the bulk ion emitter to determine the fundamental chemistry controlling the ion formation process. To develop understanding of these processes it is necessary to accurately model the motion of ions in electric/magnetic fields. The ongoing development of mathematical algorithms for the computer modeling of ion optic systems has resulted in a widely used code which is updated every few years. [1.0 FTE]

**Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720**

Applied Science Division \$210,000

100. Repetitively Pulsed Laser: Material Interaction

Russo, R.E.
Comm. 415-486-4258; FTS 451-4258

A comprehensive program is under way to study the mechanisms that describe the explosive removal of material induced by high-power pulsed-laser irradiation. For chemical separations and analysis, laser sampling can provide direct solid analysis, simultaneous multielement analysis, microanalysis, and spatial characterization. Acoustic monitoring, optical probe beam deflection, and atomic emission spectroscopy are studied to indicate distinct mechanisms occurring during the interaction. Piezoelectrics are used to study the propagation of acoustic waves induced in the material by pulsed laser irradiation. Changes in the acoustic response are studied to indicate the existence and time dependence for mechanisms of heating, melting, vaporization, and ablation. Optical probe beam deflection is employed to monitor the region adjacent to the solid surface to determine heating and cooling rates, the onset of material removal, and the formation of a laser initiated surface plasma. Atomic emission spectroscopy is used to

monitor the composition and quantity of the laser-sampled material. This material is transported to an inductively coupled plasma (ICP) for excitation to emission. By drawing correlations between these acoustic, deflection, and atomic emission data, fundamental mechanisms describing the interaction of pulsed laser radiation with solid material can be elucidated. [1.7 FTE]

Oak Ridge National Laboratory Oak Ridge, TN 37831-6365

Analytical Chemistry Division \$1,881,000

101. R & D in Secondary Ion Mass Spectrometry

Christie, W.H.; Todd, P.J.; Rosseel, T.M.
Comm. 615-576-4839; FTS 626-4839

The objective of this research is to gain a better understanding of sputtering and secondary ionization as it applies to secondary ionization mass spectrometry (SIMS). Both inorganic and organic SIMS and application to surface, depth, bulk, isotopic ratio, and imaging problems are of interest. The yield and chemistry of secondary ions and sputtered neutrals are dominated by matrix effects, often in a complementary way. In the inorganic work, changes in the behavior of secondary ions and sputtered neutrals are studied as source conditions are changed. A current application area is the site-specific chemical behavior and mass transport of inorganic pollutants in soil, rock, and other environmental matrices. A new Cameca IMS-4f ion microscope/microprobe is used to study variations in metal and isotope content in mineral grains of environmental importance. In organic SIMS, compounds are fragmented or modified chemically upon ion bombardment. Tandem mass spectrometry (MS/MS) is used for organic imaging and surface analysis. This approach mitigates matrix effects in organic SIMS by its ability to characterize ions by both m/z ratio and structure. This research is applicable to many current technical problems in materials science, health science, and environmental and waste technology. [2.2 FTE]

102. Mass Spectrometry R & D for Organic Analyses

Glish, G.L.; McLuckey, S.A.; Van Berkel, G.J.; Goeringer, D.E.
Comm. 615-574-2456; FTS 624-2456

The objective of this work is the development of new and improved methods for the analysis of organic molecules via mass spectrometry. One aspect of this involves the study of gas-phase ion chemistry and physics. By better understanding the fundamental processes involved in the various aspects of mass spectrometry experiments, analytical methods can be developed based on a solid framework of knowledge. Some of the processes of interest are ionization, unimolecular and bimolecular reactions, and ion activation. Several areas within the realm of ionization are being studied. These include electrospray ionization, glow discharge ionization, positron ionization, and ionization by controlled ion/molecule reactions. In the area of ion activation the fundamentals of collisional activation at various energies and under different instrumental conditions, along with surface-induced dissociation and photodissociation are of interest. The knowledge

gained from this work is used to improve the analytical methods and techniques used in mass spectrometry. This will help improve the methods for analyzing organic molecules and the methods for studying the gas-phase ion chemistry and physics of molecules. [2.6 FTE]

103. Advanced Spectroscopic Methods for Chemical Analysis

Hulett, L.D.; Grant, B.C.; Dale, J.M.
Comm. 615-574-8955; FTS 624-8955

Studies have been done of the ionization of large molecules by slow positrons supplied by the Oak Ridge Electron Linear Accelerator (ORELA) facility. Positrons were remoderated and injected with variable energy into a Penning trap, where they were allowed to collide with gas molecules. The ions produced were expelled from the trap and their masses were determined with a specially designed time-of-flight (TOF) spectrometer. As of this date, three different energy-dependent mechanisms of ionization molecules by positrons have been observed. Mass spectra of ions produced by positrons have been studied for over 20 different large molecules. The mass spectrometer that was specially designed for this work has a sensitivity much greater than that of the conventional TOF instruments. It has advantages for conventional mass spectrometry as well as for this work. Future work will include positron interaction with solid surfaces, studying stimulated desorption, and positron annihilation at defect sites. Work accomplished in heavy ion induced satellite emission (HIXSE) is reported. This research involves personnel from Vanderbilt University and State University of New York, Fredonia, as well as those of Oak Ridge National Laboratory. [2.8 FTE]

104. Research Development and Demonstration of Advanced Chemical Measurement Techniques

Ramsey, J.M.; Shaw, R.W.; Whitten, W.B.; Young, J.P.
Comm. 615-574-5662; FTS 624-5662

The objective of this research program is to develop techniques for spectrochemical analysis with enhanced specificity and sensitivity. This project involves a number of experimental efforts including work on new laser sources, measurement schemes, and sampling techniques. Applications of semiconductor diode lasers to high-resolution optical spectroscopy are being studied. Advances in this area may find application in the area of field-portable instrumentation using laser-based measurement schemes. Resonance-enhanced multiphoton ionization (REMPI) spectroscopy is employed in several experiments for high-resolution, high-sensitivity measurements. These experiments include resonance ionization mass spectrometry (RIMS) in magnetic sector instruments and ion trap mass spectrometers. The RIMS experiments are primarily directed toward isotope ratio measurements. New techniques for ultrasensitive fluorescence analysis of solutions are being studied. These techniques are based on performing fluorescence spectroscopy on microdroplets suspended in electrodynamic traps. Electrodynamic traps are also being used to study solid-phase microparticles using a combination of optical and mass spectrometry. The measurement techniques being

developed have broad application to such areas as environmental monitoring, global environmental studies, and biotechnology. [3.0 FTE]

105. Mass Spectrometric R & D for Inorganic Analyses

Smith, D.H.; McMahon, J.M.; Van Berkel, G.J.
Comm. 615-574-2449; FTS 624-2449

The objective of this work is to advance the state of the art in inorganic mass spectrometry. Improvements are sought in both instrumentation and sample preparation methodology in order to gain enhanced precision, accuracy, specificity, and sensitivity. Isotope dilution techniques are used extensively. Improved methodology for determining various difficult-to-measure elements is being developed. For improved sensitivity and more accurate measurements in survey analyses, new work is under way in glow-discharge mass spectrometry. Its ability to deliver quantitative results over a wide dynamic range is being evaluated with respect to the effect of sample matrix. Its ability to measure isotopic ratios is presently being evaluated, and a radio frequency (rf) probe for analysis of nonconducting samples is being developed in collaboration with researchers at Clemson University. [2.3 FTE]

Chemical Technology Division **\$1,278,000**

106. Chemical and Physical Principles in Multiphase Separations

Byers, C.H.; Basaran, O.A.; Scott, T.C.
Comm. 615-574-4653; FTS 624-4653

This project comprises several fundamental studies that address the use of electromagnetic fields to enhance the effectiveness of multiphase separation processes. The primary focus of the program is analysis of effects of electric fields on droplets, with the resulting information to be used for devising means to dramatically improve transport rates in liquid-liquid systems. This thrust addresses such issues as drop formation, stability, oscillation, breakup, and coalescence in electric fields. A secondary focus is examining the use of high-intensity, high-gradient (HIHG) magnetic fields in separations processes. This investigation involves the study of the interactions of charged macromolecular entities in viscous media which are under the influence of HIHG magnetic fields. A third, more recent thrust is exploring the use of electric fields in enhancing liquid-vapor operations. Some key issues here are to develop a better understanding of (1) the effects of external fields on bubbles in particular and polarizable media in general and (2) the fluid dynamics of bubbly liquids. [2.8 FTE]

107. Interactions of Solutes, Solvents, and Surfaces: Adsorption and Supercritical Extraction

Cochran, H.D.; Byers, C.H.
Comm. 615-574-6821; FTS 624-6821

Fundamental theoretical and experimental studies are aimed at understanding the striking properties of supercritical solutions in terms of the underlying fluid microstructure and molecular interactions. These solutions are important in novel separation technologies such as supercritical extraction and supercritical fluid chromatography. Molecular dynamics simulation studies have been

completed of supercritical water and of solutions in supercritical waters, for the first time revealing the hydrogen-bonding structures surrounding different solute molecules in supercritical aqueous solution. After derivation of a new theoretical model to predict the effect of a third component (e.g., an added cosolvent or a second solute) on the solubility of a solute in a supercritical solvent, work continues to test the usefulness of the new theory for practical calculations. Direct measurement of the local fluid microstructure surrounding a solute in a supercritical solvent is the goal of planned neutron scattering experiments; the apparatus for this work has been designed and fabricated and is undergoing testing in the laboratory. The new technique developed for calculating chemical potential in supercritical solutions from molecular distribution functions can soon be tested with the expected results of new Monto Carlo molecular simulations of supercritical solutions in the grand canonical ensemble. [1.0 FTE]

108. Chemistry of Actinides and Fission Products

Toth, L.M.
Comm. 615-574-5021; FTS 624-5021

The primary purpose of this project is to explore the fundamental chemistry of the actinide elements and their fission products. Emphasis is placed on the photochemistry, coordination chemistry, and separations chemistry of these elements, especially as they relate to problems in waste management, environmental control, and the nuclear fuel cycle. The chemistry of other elements is often examined in parallel with that of the actinides and fission products in order to develop a better understanding of the periodic behavior of the elements. The current interests are (1) low-temperature spectroscopy/photochemistry (including matrix isolation methods to isolate and identify reactive intermediates) and (2) neutron/X-ray small-angle scattering experiments of hydrolytic polymers (to define sizes and geometries of colloidal species and those factors controlling their formation, reactivity, and ultimate size). [1.5 FTE]

Chemistry Division **\$882,000**

109. Chemical and Structural Principles in Solvent Extraction

Moyer, B.A.; Sachleben, R.A.; Burns, J.H.
Comm. 615-574-6718; FTS 624-6718

The general purpose of this task is to elucidate the basic thermodynamic and structural principles governing solvent-extraction and related separation techniques of relevance to energy technologies. Major questions of interest pertain to the cooperativity of extractant functionalities in providing suitable coordination environments for metal cations. To provide insight into such questions, model extractants are designed, synthesized, and tested for separation efficacy. Extraction measurements are interpreted by computer-aided equilibrium analysis, X-ray structure determination of crystalline model compounds, molecular mechanics, spectroscopy (e.g., FTIR, NMR, UV/vis, and Raman), and other physical measurements. An important thrust concerns the question of how most or all of the functionalities needed for the recognition and extraction of alkali metal cations may be incorporated into one extractant molecule, as represented

by the class of ionizable dibenzo-14-crown-4 lariat ethers. Selectivity principles applicable to the separation of transition and alkaline earth metals are under investigation for systems containing polydentate oxa and thia ligands combined synergistically with organophilic sulfonic and carboxylic acids. Through extensive modeling of extractions involving a representative sulfoxide extractant, new insight into underlying equilibria is being gained. Host-guest interactions are being probed in the analysis of the hydration of crown ethers. [4.2 FTE]

Pacific Northwest Laboratory Richland, WA 99352

Chemical Sciences Department \$1,279,000

110. Analytical Mass Spectrometry Research

Baer, D.R.; Hubbard, C.W.; Styris, D.L.
Comm. 509-376-1907; FTS 444-1907

This project generates new knowledge important to the field of mass spectrometry and develops techniques to improve and expand the applications in this field. The project presently consists of two parts: (1) research to elucidate and predict the properties of new surface ionization source materials and (2) research directed toward the fundamental understanding and development of new mass spectrometric techniques. Research into the properties of new surface ionization materials explores the effects of surface impurities on work functions in order to model the surface ionization efficiencies of new materials. The electronic behavior of composite rhenium surfaces containing nickel and copper is being investigated by surface work function measurements, Auger electron spectroscopy, and ultraviolet photoelectron spectroscopy. Models developed from these data will be used to predict behavior of other couples which will then be fabricated and tested experimentally. The research to provide understanding and development of new mass spectrometric techniques addresses a broadly applicable mass spectrometry based on using a single source for both thermal atomization and electron impact ionization. [2.1 FTE]

111. Laser-Based Analytical Techniques

Miller, R.J.; Cannon, B.D.
Comm. 509-375-2968

The objective of this program is to provide new knowledge necessary for development of improved analytical methods that exploit advanced laser technologies. Analytical methodologies affording high selectivity and extreme sensitivity are needed for many energy technologies. The proposed research will address spectroscopic characterization of specific atomic, molecular, and ionic species, and studies of underlying chemical and physical phenomena. Electron attachment from Rydberg atoms is proposed as an efficient, gentle source for negative ion mass spectroscopic analyses of complex environmental mixtures. Studies will characterize Rydberg states of alkali metals and their decay dynamics. Electron attachment cross sections will be measured for prototype molecules as functions of collision and electron binding energies. This new knowledge will enable efficient preparation of negative ions for analytical applications. Reactive intermediates generated during high-energy processing of toxic organic wastes will be studied. High-resolution laser spectroscopy

will characterize the structures and dynamics of radicals and molecular ions produced within flames and plasmas. This new knowledge will enable better diagnostics of the chemistry of flames and plasmas and improved waste disposal technologies. [1.2 FTE]

112. Fundamental Phase Partitioning in Supercritical Fluid Chromatography

Smith, R.D.; Yonker, C.R.; Fulton, J.L.
Comm. 509-376-0723; FTS 444-0723

The goal of this project is to obtain fundamental information on the kinetic, thermodynamic, and molecular level phenomena related to structure in supercritical fluid solutions. Understanding these phenomena will lead to new supercritical fluid separation and reaction processes, and will suggest new approaches for improving existing processes. The scope of these studies spans the range from (1) simple bimolecular solute/solvent interactions to (2) more complex multimolecular clustering and aggregation phenomena, as well as (3) fluid/liquid interfacial phenomena. In the most general sense, this project is exploring supercritical fluid phenomena in order to bridge the gap between the understanding of the gas and liquid states. The approach entails use of spectroscopic techniques such as FT-IR and Raman spectroscopy, small angle X-ray scattering (SAXS), and dynamic fluorescence quenching (DFQ). Concurrent are efforts to model the fluid structure (using statistical mechanics) and to predict intermolecular and interaggregate attractive potentials (based upon *ab initio* calculations). A main area of study involves the formation organized molecular assemblies (e.g., micelles and microemulsions) in supercritical solutions; a potential basis for new separation and reaction processing methods. The pressure-dependent effects on the fluid structure are being measured spectroscopically and predicted theoretically. Light- and neutron-scattering studies are exploring the microemulsion structure and the nature of the attractive (i.e., micelle-micelle) interactions in fluids, providing new insights into the forces dictating the phase behavior of these systems. It is anticipated that this program will provide the basis for new and improved analytical separations (i.e., extractions and chromatography) and for larger scale separations and reactions as well as expanded understanding of solvation and structure in both the supercritical and liquid phases. [1.6 FTE]

113. Mechanisms of High-Temperature Atomization in Chemical Analysis

Styris, D.L.
Comm. 509-376-1907; FTS 444-1907

This project uses mass spectrometry and atomic absorption spectrometry techniques to help elucidate mechanisms that control high-temperature surface induced atomization; unique applications of these surfaces are developed and refined. These mechanisms are providing the basis needed to broaden and improve applications of spectrometries that rely on thermal atomization sources. The gas-phase species created by these high-temperature surfaces during rapid thermal ramping *in vacuo* and at atmospheric pressure are monitored in real time. Condensed-phase species are being investigated by EXAFS spectroscopy. Surface state theory and available thermodynamic and kinetic data are then used to help identify and characterize the controlling chemical and physical processes. Mechanisms associated with the

unique hollow-anode plasma furnace atomization non-thermal excitation spectroscopy source, developed on this project, are also being investigated through emission spectrometry. The work primarily involves pyrolytic graphite surfaces because of the extensive use of this material for thermal atomization sources. However, atomization on high-temperature quartz surfaces, such as those used in hydride generation spectroscopy, has also been investigated. Data essential to establishing the validity of existing models is provided by investigations of atomization of yttrium and of Group III-B elements. A unique two-step furnace vaporization system is providing controlled vaporization and atomization in order to quantify preatomization losses that are identified by the mass spectroscopy. [1.0 FTE]

Heavy Element Chemistry

Argonne National Laboratory Argonne, IL 60439

Chemistry Division **\$1,726,000**

114. Heavy Element Chemistry Research
Morss, L.R.; Appelman, E.H.; Beitz, J.V.; Carnall, W.T.; Soderholm, L.; Sullivan, J.C.
Comm. 708-972-3667; FTS 972-3667

The project objectives are (1) to determine the electronic and bonding properties of the actinide and related elements, (2) to elucidate their chemical behavior, and (3) to develop a predictive understanding of the reactivity and energy-transfer processes in inorganic species. Syntheses of transuranium oxides and halides, and of powerful oxidants and fluorinating agents such as hypofluorous acid, are coupled with structural, spectroscopic, and thermochemical measurements to determine reactivity mechanisms and stability limits of these species. Electronic-structure, photophysics, and photochemistry studies of f elements provide insights into the chemical consequences of excited-state formation and the dynamics of relaxation modes in solids, solutions, and gases. Laser-induced fluorescence and photoacoustic spectroscopy, coupled with microchemical sample preparations, achieve ultrafast and ultrasensitive detection and characterize and interpret energy transfer processes of transuranium species. Thermodynamic and kinetic properties of electron transfer and complex-formation reactions of transuranium ions in solution are determined by stopped-flow and temperature-jump instrumentation. Bonding of complex actinide species in solution is interpreted by X-ray absorption and nuclear magnetic resonance spectroscopies. Relationships between the electronic structure of f elements in solids, and properties such as crystal structure and magnetic susceptibility, are interpreted as a function of the nature, distance, and symmetry of neighboring ions. Cooperative properties such as magnetic ordering and superconductivity are modeled using insight gained from techniques such as resistivity, Mössbauer spectroscopy, and inelastic neutron scattering. [7.4 FTE]

Lawrence Berkeley Laboratory University of California Berkeley, CA 94720

Chemical Sciences Division **\$1,280,000**

115. Actinide Chemistry
Edelstein, N.M.
Comm. 415-486-5624; FTS 451-5624

Development of new technological processes for the use, safe handling, storage, and disposal of actinide materials relies on the further understanding of basic actinide chemistry and the availability of a cadre of trained personnel. This research program is a comprehensive, multifaceted approach to the exploration of actinide chemistry and to the training of students. Research efforts include (1) synthetic organic and inorganic chemistry for the development of new chemical agents and materials; (2) the chemical and physical characterization through such techniques as X-ray diffraction, optical and vibrational spectroscopy, magnetic resonance and susceptibility; and (3) thermodynamic and kinetic studies for the evaluation of complex formation. One aspect is the development and understanding of complexing agents that specifically and effectively sequester actinide ions. Such agents are intended for the decorporation of actinides in humans, in the environment, and in systems related to the nuclear fuel cycle. Extensive studies are under way to prepare organometallic and coordination compounds of the f-block elements that show the differences and similarities among the f-elements, and between the f- and d-transition series elements. Optical and magnetic studies on actinides as isolated ions in ionic solids, and in molecules, provide information about electronic properties as a function of atomic number. [12.0 FTE]

Nuclear Science Division **\$130,000**

116. Chemistry of the Heaviest Elements
Hoffman, D.C.
Comm. 415-486-4474; FTS 451-4474

The objective of this project is the determination of the fundamental chemical properties of the heaviest elements to determine the architecture of the periodic table of the elements at its furthest reaches and to assess the influence of relativistic effects on these chemical properties. The actinide series ends with Lr (element 103) and the change in chemical properties in going to the transactinide elements, Rf (104), Ha (105) and (106), is especially important. A program to investigate some of the most basic chemical properties of elements 102 through 106 is being undertaken. This includes the determination of range and stability of oxidation states, measurement of ionic radii, and anionic halide complex formation. Atoms of the heaviest elements are produced at the LBL 88-inch Cyclotron by irradiation of heavy actinide targets, such as ^{248}Cm , ^{249}Bk , or ^{249}Cf . These chemical properties can be determined using "atom-at-a-time" techniques. The aqueous and gas phase chemistry of Rf and Ha has been investigated using 65-seconds ^{261}Rf and 35-seconds ^{262}Ha . In recent experiments, a multinational collaboration used computer-controlled automated systems to compare the volatilities of their bromides and chlorides with those of

their lighter homologs in groups 4 and 5 of the periodic table to perform detailed studies of the anionic chloride complexes of Ha and its group 5 homologs and Pa. Unexpected deviations in properties from predictions based on periodic table trends were observed. These studies demonstrate that the chemical properties of the transactinides cannot be reliably extrapolated from the trends exhibited by their lighter homologs and that additional experimental and theoretical work will be required in order to gain a better understanding of their complex chemistry. [1.0 FTE]

**Los Alamos National Laboratory
University of California
Los Alamos, NM 87545**

Isotope and Nuclear Chemistry Division **\$358,000**

117. Actinide Chemistry in Near-Neutral Solutions

Hobart, D.E.

Comm. 505-667-9313; FTS 843-9313

The project objective is to provide fundamental physico-chemical knowledge pertinent to the behavior of plutonium and other actinides under environmental and physiological near-neutral pH conditions. In spectral studies of plutonium dioxide, a new absorption band has been discovered and attributed to a phonon or vibronically coupled f-f transition. This new spectral feature may have important significance in Pu(IV) electron energy level calculations. Thorium and uranium silicates have been prepared by a hydrothermal method, and characterization of naturally occurring actinide silicate minerals is progressing. Carbon-13/oxygen-17 NMR studies are continuing in the efforts to determine the carbonate complexation quotients for Pu(IV). Preliminary experiments performed with U(VI) carbonate complexes were successful. Application of X-ray absorption spectroscopy (XAS) for actinide speciation has continued and is being expanded to study Pu(IV) colloid. Advances in the spectroscopy of model complexes include obtaining the electronic spectra of some synthetically prepared and structurally well-characterized thorium and uranium alkoxide complexes. These baseline spectra, when added to a larger database, are expected to permit identification of unknown actinide species in the environment. [0.6 FTE]

118. Actinide Organometallic Chemistry

Sattelberger, A.P.; Burns, C.J.

Comm. 505-667-4457; FTS 843-4457

The project objective is to study fundamental aspects of early actinide organometallic chemistry. The current focus is on: (1) the synthesis and characterization of new classes of early actinide complexes containing nonclassical ligands, such as alkyls, amides, alkoxides, imides, phosphides, phosphinidenes, and thiolates; (2) investigations of actinide-mediated reactions of unsaturated inorganic and organic substrates; (3) variable temperature magnetic and electronic spectroscopic studies; (4) actinide alkoxide and oxo/alkoxide complexes as models for aqueous-phase hydroxo and oxo/hydroxo species; (5) the development of low-temperature solution and gas-phase routes to solid-state actinide materials. Recent results include (1) the

structural characterization of $(C_5Me_5)UI_2(THF)_3$, a versatile starting material in uranium(III) organometallic chemistry; (2) the preparation of crystalline Lewis base adducts of thorium tetrabromide and thorium tetraiodide; (3) the synthesis and structural characterization of a variety of thorium(IV) alkoxide complexes, including $Th_4(O-i-Pr)_{16}(py)_2$; (4) the synthesis and structural characterization of $(C_5Me_5)_2UP(SiMe_3)SiMe_2CH_2$, the first actinide phosphacycle; and (5) the first example of α -hydrogen elimination from a uranium(IV) complex in the transformation of $\{[(Me_3Si)_2N]_3UN(H)Ar\}$ to $\{[(Me_3Si)_2N]_2U(\mu-NAr)\}_2$. [0.7 FTE]

Nuclear Materials Technology Division **\$124,000**

119. Actinide High-Temperature Thermodynamics

Kleinschmidt, P.D.

Comm. 505-667-6945; FTS 843-6945

Thermochemical parameters of the actinide fluoride and chloride systems are measured using Knudsen effusion mass spectrometry. The thermochemical quantities enthalpy, entropy, and free energy are derived from experimentally measured pressures and equilibrium constants. The goal of this program is to determine the effects 5f electrons have on chemical bonding in the actinide series. The strength of the bonding is reflected in thermochemical parameters such as the enthalpy of formation. Both molecules and solid phases are investigated with this approach. Specific systems being investigated include the neptunium, plutonium, americium, and californium fluorides. Bond dissociation energies and heats of sublimation are measured for these systems as well as ionization potentials of the gaseous molecules. The free energy of mixing of mixed salts of $PuCl_3$ with the group IA chlorides is also being measured. Use of this data in the analysis of waste storage and disposal, scrap recovery, radioisotope heat sources, metal production, and waste minimization are examples of practical applications. [0.5 FTE]

**Oak Ridge National Laboratory
Oak Ridge, TN 37831**

Chemistry Division **\$1,236,000**

120. Chemistry of Transuranium Elements and Compounds

Moyer, B.A.; Gibson, J.K.; Johnson, E.;

Haire, R.G.; Krause, M.O.; Peterson, J.R.

Comm. 615-574-6718; FTS 624-6718

An understanding of the chemistry and physics of the transuranium elements is being sought through determination of key thermodynamic, structural, and electronic properties of the actinides as a function of electronic configuration. Experimental quantities of the elements Cm through Fm produced in the High Flux Isotope Reactor are central to extending studies across the 5f series. Unique information on 5f orbital bonding in transplutonium metals, alloys, and compounds is being obtained by application of sufficient pressure to produce structural and electronic transitions, including delocalization of

valence electrons. To probe the high-temperature thermochemical properties of actinides in high oxidation states such as found in Am fluoride and Cf oxide systems, mass spectral techniques are being employed. Insight into the tetravalent state is also being derived from aqueous calorimetric measurements of the enthalpies of dissolution of Cm and Cf mixed oxides. By use of relativistic quantum mechanics, the ionization potentials, atomic radii, ionic radii, and derived thermodynamic properties of elements 104 and 105 are being calculated. Information on solid-state structure of actinide halides, oxides, and coordination compounds is being obtained from phonon Raman and luminescence spectroscopies. In planned experiments, the electronic structure of the actinides will be probed by photoelectron spectrometry. [5.8 FTE]

Chemical Engineering Sciences

**Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720**

Applied Science Division **\$342,000**

121. Turbulent Combustion

*Talbot, L; Cheng, R.K.
Comm. 415-642-6780*

The interaction between fluid mechanical turbulence and chemical reactions in laboratory-scale premixed and non-premixed turbulent flames is studied experimentally using laser diagnostic techniques. A theoretical/numerical study of premixed turbulent flames using the vortex dynamics method is also being conducted. The objective is to obtain a better understanding of the fundamental physical processes controlling turbulence-combustion interactions. Such knowledge is basic to the development of theories that can address a variety of practical combustion problems that are relevant to combustion efficiency and pollutant emissions. At present, experiments are focused on studying flame conditions with fluid mechanical time scales much larger than those of chemical reactions. Simplified theoretical treatment of these flames is possible and several models have been developed that need experimental validation and verification. The experiments are focused on obtaining space and time resolved statistical data of scalar and velocity fluctuations to study the effects of large heat release on the turbulent flow field, and using planar laser imaging techniques such as high speed cine tomography to determine the scales of the flame structures. The statistical data are compared with model predictions in addition to determining the effects of turbulence intensity on the burning rates and heat release on the flowfield. The tomographic data are analyzed by the fractal technique to investigate the spatial scales of the flame. These scalar scales are directly related to the burning rate of premixed turbulent flame under these experimental conditions and are the source terms in many theoretical models. [3.0 FTE]

Chemical Sciences Division **\$167,000**

122. Molecular Thermodynamics for Phase Equilibria in Mixtures

*Prausnitz, J.M.
Comm. 415-642-3592*

Phase equilibria are required for design of efficient large-scale separation processes (e.g., distillation and extraction) in the chemical and related industries. In this context, "efficient" refers to optimum use of raw materials and to conservation of energy. Since the variety of technologically important fluid mixtures is extremely large, it is not possible to obtain all equilibria from experiment. Therefore, the objective of this research is development of molecular thermodynamics for interpretation and correlation of reliable experimental data toward confident prediction of phase equilibria for engineering. The correlations are expressed through semitheoretical physicochemical models in a form suitable for computer-aided design. Particular attention is given to those materials that may be useful for innovative low-energy consuming separation processes such as polymers and gels and micellar systems with possible applications in biotechnology. However, attention is also devoted to conventional materials for applications in fuel technology and for recovery of solutes from wastewater. Development of molecular thermodynamics calls for a combination of theoretical, computational, and experimental work. Further, it requires simultaneous awareness of progress in molecular science and of realistic requirements for engineering design. [2.75 FTE]

**Los Alamos National Laboratory
University of California
Los Alamos, NM 87545**

Theoretical Division **\$85,000**

123. Thermophysical Properties of Mixtures

*Erpenbeck, J.J.
Comm. 505-667-7195; FTS 843-7195*

The thermophysical properties of mixtures of particles interacting through simple interaction potentials are evaluated, using both equilibrium Monte Carlo (MC) and molecular dynamics (MD), as well as nonequilibrium molecular dynamics. The properties under investigation include the equation of state and transport properties, including mutual and self diffusion, shear and bulk viscosity, thermal conductivity, and thermal diffusion. Fundamental questions arising in the theory of fluids and fluid mixtures are addressed where numerical "experiments" are appropriate. MCMD calculations have been extended to 50-50 binary hard-sphere mixtures having mass and diameter ratios relevant to helium-xenon mixtures. At a moderate fluid density, these yield a mutual diffusion coefficient 7% below, thermal conduction and thermal diffusion coefficients 3% below, and a shear viscosity 2% above the Enskog-theory predictions. These estimates include extrapolations to the infinite system limit as well as long-time tail corrections. A model of diatomic molecules has been shown to exhibit vastly different behavior with respect to the sharing of energy between the vibrational and translational motion, depending on whether the intermolecular interaction is

impulsive or soft. In both cases, systems of too few molecules have dynamical trajectories which are regular rather than chaotic, so that statistical mechanics does not apply. For large numbers of molecules, the systems behave ergodically, but the time constant for energy exchange grows rapidly with vibrational frequency for a soft interaction but remains well behaved for impulsive interactions. [0.5 FTE]

Sandia National Laboratories, Livermore
Livermore, CA 94551-0969

Combustion Research Facility **\$364,000**

124. Analysis of Turbulent Reacting Flows

Ashurst, W.; Kerstein, A.R.; Barr, P.K.

Comm. 415-294-2274; FTS 234-2274

The goal of this project is to develop numerical simulation techniques for the understanding of reacting turbulent flows. The objective is to show the mechanisms of turbulent mixing and reaction. Numerical simulation of unsteady reacting flow places an emphasis on flame-vortex interactions using the vortex dynamics method

and/or direct numerical simulations of the Navier-Stokes equations. Calculations of three-dimensional Navier-Stokes flow combined with a field equation for constant density premixed flame propagation reveal that the prominent flame shape is that of a cylinder, reflecting the tube-like nature of the intense vorticity. The probability of surface geometry will guide future calculations with realistic chemistry. Vortex dynamics simulations of a pulse combustor have shown, by comparison with experiment, that strain rate quenching of a premixed flame is a key in the energy release rate, which governs the successful operation of these combustors. The linear-eddy mixing model, unique in its representation of the distinct influences of convective stirring and molecular diffusion, has been applied to turbulent jet diffusion flames and has provided interpretations of measured structure based on the interplay of molecular mixing, thermochemistry, and buoyant entrainment processes. Results from these tasks will contribute to the basic understanding of turbulent reacting flows, assist in planning experiments, and aid in interpreting experimental data at the Sandia Combustion Research Facility (and elsewhere), and improve capabilities for predictive modeling of reacting flows in practical geometries. [1.7 FTE]

OFFSITE INSTITUTIONS

Photochemical and Radiation Sciences

University of Akron
Akron, OH 44325

Department of Chemistry

125. Dynamics of Charge Transfer Excited States Relevant to Photochemical Energy Conversion

Lim, E.C.

\$100,000

Comm. 216-972-5297

The primary objective of the research program is to gain fundamental understanding of the factors governing the efficiency of charge transfer processes in molecular systems of relevance to photochemical energy conversion. Current emphasis is on the study of intramolecular charge separation and charge neutralization in bichromophoric systems of the general structure M-X-M, where two identical aromatic moieties (M) are joined by a single bridging group X(= CH₂, NH, O, SiH₂, and so forth). Novel biphotonic, as well as more conventional monophotonic, laser excitation schemes are used to create intramolecular charge transfer states in these species. The time- and energy-resolved spectra of these states are then probed by laser kinetic spectroscopy to identify the rate and mode of their decays. The photoisomerization of van der Waals complexes into the corresponding exciplexes are also being investigated in a supersonic free jet for the purpose of probing the factors that influence the efficiency of the conformational isomerization related to the excited-state charge transfer process.

University of Alabama
Tuscaloosa, AL 35487

Department of Chemistry

126. Magnetic Resonance and Optical Spectroscopic Studies of Carotenoids

Kispert, L.D.

\$83,446

Comm. 205-348-7134

The objectives of this research are to understand the role of a host matrix in the mechanism of carotenoid cation radical formation and decay and to determine the special properties of carotenoids that enable them to serve both as antennae and as photoprotective agents in photosynthesis and as a possible component of electron transfer processes. Studies of carotenoids have shown that the first excited singlet state lifetime of β -carotene equals 10 picoseconds and lengthens as the conjugated chain length decreases. The short lifetime is a result of nonradiative decay mechanisms within the carotenoids. Simultaneous

electrochemical and electron paramagnetic resonance (EPR) measurements indicate that upon oxidation of canthaxanthin, 96% carotenoid cation radicals are formed while 99.7% dications are formed upon the oxidation of β -carotene, suggesting a reason for the EPR observation of carotenoid radicals in some photosystems and not others. Semiempirical molecular orbital calculations of the minimum energy structure of the carotenoid cation radicals, singlet and triplet excited states, have been completed and are being used to interpret EPR and electron-nuclear double resonance measurements. Attempts are under way to manipulate the host matrix in such a manner as to understand the carotenoid function (i.e., protection, quenching, energy transfer, and antenna) and to ultimately develop predictive mechanisms for directing the outcome of photochemical events.

Arizona State University
Tempe, AZ 85287

Department of Chemistry

127. Photoinitiated Electron Transfer in Multichromophoric Species—Synthetic Tetrads and Pentads Featuring Diquinone Moieties

Gust, J.D., Jr.; Moore, T.A.;

\$159,000

Moore, A.L.

Comm. 602-965-4547

The project objective is the synthesis and study of complex four- and five-part molecular devices that mimic natural photosynthetic reaction centers. Results of these investigations will aid in the design of artificial solar energy harvesting systems, increase understanding of natural photosynthesis itself, and provide an entry into the developing field of molecular electronics. For example, a molecular pentad C-P_{Zn}-P-Q-Q has recently been synthesized. It consists of a diporphyrin moiety (P_{Zn}-P) linked to a carotenoid polyene (C) and a diquinone species (Q-Q). Absorption of light by the molecule results in photoinitiated electron transfer to produce an initial charge-separated state C-P_{Zn}-P⁺-Q⁻-Q with a quantum yield of 0.85. A series of subsequent electron-transfer steps leads to a final charge-separated state C⁺-P_{Zn}-P-Q-Q⁻ with an overall quantum yield of ~0.83. This species has a lifetime of 55 μ s, and has stored within it about one-half of the energy of the absorbed photon. The knowledge gained from studies of the pentad and simpler molecules is being used to design a new generation of pentad and tetrad molecules in which the quantum yield, lifetime, and amount of stored energy will be further optimized. In addition, these molecular devices are being incorporated into monolayers and other thin films in order to investigate their photoelectrochemical properties.

University of Arizona
Tucson, AZ 85721

Department of Biochemistry

- 128. Photochemical Energy Conversion by Membrane-Bound Photoredox Systems**
Tollin, G. **\$110,000**
Comm. 602-621-3447

Mechanisms of photochemical electron transfer in chlorophyll-containing lipid bilayer vesicles are being investigated using laser flash photolysis and electrochemical techniques. Current effort is being spent on developing strategies for use of redox proteins as electron donors and acceptors, and on studies of the mode of interaction of such proteins with lipid bilayers using nuclear magnetic resonance (NMR) and cyclic voltammetric methods. Kinetic measurements and time-resolved difference spectra are used to elucidate the sequence of electron transfer and the reaction mechanisms. Both peripherally bound redox proteins (e.g., plastocyanin, cytochrome *c*, and ferredoxin) as well as integral membrane proteins (e.g., cytochrome oxidase) are being investigated. Present studies use systems that carry out vectorial electron transport across the bilayer between redox protein donors and acceptors and those carrying out multistep electron transfers involving quinone or viologen mediators and several redox proteins in a linear or cyclic sequence. The primary goal is to achieve conditions in which light energy is efficiently stored in redox products that can be coupled to such potentially useful systems as hydrogen generation, nitrogen fixation, and proton translocation, or to direct conversion to electricity.

Boston University
Boston, MA 02215

Department of Chemistry

- 129. Study of Intermediates from Transition Metal Excited-State Electron-Transfer Reactions**
Hoffman, M.Z. **\$100,000**
Comm. 617-353-2494

Coordination complexes of Ru(II), especially those possessing aromatic α -diimine ligands, play an important role as photosensitizers in model photochemical systems for the conversion and storage of light energy. The electron-transfer quenching of the excited state of the photosensitizer results in its one-electron oxidation or reduction, and the corresponding reduction or oxidation of the quencher. The major objective of this research, which utilizes the techniques of time-resolved spectrofluorimetry, and continuous and pulsed photolysis and radiolysis, is to gain an understanding of (1) the parameters that govern the efficiency of the formation of energy carriers from the quenching reaction; (2) the dependence of the kinetics and efficiencies of all the mechanistic steps of the overall reaction on temperature and the nature of the solution medium; and (3) the properties and reactivities of the reduced and oxidized species. During the past year, the following projects have been investigated: (1) the preparation and characterization of Ru(II)-tris-homo- and

heteroleptic complexes containing di-, tri-, and tetraazine ligands; (2) the determination of cage escape yields in the oxidative and reductive quenching of the excited states of Ru(II) complexes as a function of the energy gap between the redox products, the nature of the solution medium, and the temperature; (3) the reductive quenching of the excited states of Cr(III) complexes; (4) the acid-base, electron-transfer, and electrochemical properties of one-electron reduced Ru(II) complexes; and (5) the reductive quenching of the excited state of Ru(bpz)₃²⁺ (bpz = 2,2'-bipyrazine) by molecules of biological relevance.

- 130. Photoinduced Electron Transfer in Ordered Polymers**
Jones, G. **\$105,000**
Comm. 617-353-2498

Investigations concern the photochemistry of biopolymer systems that have been modified with covalently or electrostatically bound dye molecules. An objective of the research is the demonstration that electron transfer between bound dye and pendant groups that are native to the biopolymer can be observed and that charge migration along the polymer surface among electroactive groups is important. The efficiency of electron or hole migration along the polymer chain is expected to depend on the helicity of the biopolymers selected for study and the characteristic interaction of neighboring organic functional groups. Three dye/polymer systems have been most recently investigated. (1) Poly-L-tryptophan modified by attachment of the organic dye, eosin, at the N-terminal residue of the peptide has been studied by laser flash photolysis in terms of electron or hole transfer between the dye moiety and biopolymer side chains. (2) Several peptides have been prepared that contain electroactive (tryptophan and tyrosine) and nonelectroactive residues (alanine) which permit the spacing of electron donor and acceptor groups (including a dye conjugate) at intervals of varying distance for study of photoinduced electron transfer rates. (3) Polyelectrolytes related to polyacrylic acid have been used to electrostatically bind (heavily load) aggregates of dye molecules such as crystal violet and pseudoisocyanine; electron transfer between dye aggregates and co-bound groups on the polymer chain has been investigated. In these studies emphasis is placed on the opportunities provided with synthetic biopolymers for design of proximal groups for electron transport and the potential role of secondary structure of modified biopolymers in controlling charge separation.

Brandeis University
Waltham, MA 02254

Department of Chemistry

- 131. Mechanistic Studies of Excited State Chemical Reactions**
Linschitz, H. **\$90,000**
Comm. 617-736-2506

This program is designed to clarify the mechanisms of excited state redox reactions, in order to establish the factors controlling primary quantum yields (efficiencies) of charge separation in photochemical energy-storing reactions. These involve thermodynamic parameters (free enthalpy of the electron-transfer reaction) and kinetic

factors, including temperature, viscosity, and solvent polarity. For triplet excited states, spin-orbit coupling and mechanisms for spin relaxation within the primary reaction complex play a key role. Of particular interest are the properties of ion-paired porphyrin "dimers," which are analogues of the structures found in photosynthetic reaction centers. In addition the relation between excited state redox reactions involving electron versus hydrogen atom transfer is being studied, using donors in which both processes can occur in the primary step.

California Institute of Technology Pasadena, CA 91125

Department of Chemistry

132. Picosecond Dynamic Studies of Electron Transfer Rates at III-V Semiconductor/Liquid Interfaces

Lewis, N.S.

\$120,000

Comm. 818-356-6335

The goal of this project is to examine the fundamental aspects of energy conversion using semiconductor/liquid interfaces. A specific focus of this work is the time-resolved dynamics of interfacial charge transfer at semiconductor/liquid contacts. These processes are important because they influence the overall energy conversion efficiencies attainable with solid/liquid junction photochemical systems, and also because they allow evaluation of current electron transfer theories. Previous work has focused on two aspects of this general area: time resolved photocurrent measurements and time-resolved luminescence measurements. Transient photocurrent measurements have been performed at n-Si/CH₃OH-dimethylferrocene⁺⁰ junctions and at n-TiO₂/H₂O interfaces. Current transients in these systems have been found to decay quite rapidly; this process has been interpreted previously to represent either charge transfer across the solid/liquid interface or simply discharging of the space charge capacitance through the measurement circuit and the photoelectrochemical cell. The data on the n-Si system support the latter interpretation, and indicate that such dynamic measurements are not very useful in elucidating interfacial charge transfer dynamics. A second aspect of previous work has focused on mechanistic issues relating to time-resolved luminescence decays at semiconductor/liquid interfaces. If proper samples are utilized, these luminescence decays can be indirectly used to provide information on the interfacial charge transfer dynamics. Such experiments have been performed on GaAs/liquid contacts, both to explore rate constants for charge transfer and to elucidate mechanisms of charge transport in important photoelectrochemical cell configurations. Currently, the theory for these decays is being elucidated, and the combination of the luminescence and photocurrent decay procedures are being applied to elucidate the features of light-induced charge flow at semiconductor/liquid contacts.

University of California, Berkeley Berkeley, CA 94720

Department of Chemistry

133. Theoretical Studies of Electron Transfer in Complex Media

Chandler, D.

\$110,000

Comm. 415-643-6821

(14 months)

The structures, dynamics, and free energies of the transition states for the prototypical aqueous ferrous-ferrous electron-transfer reaction have been determined by computer simulation through application of a novel sampling procedure. The research on this system is concerned with (1) algorithm development for simulating the quantum dynamics for evolution initiated at the transition states; (2) derivation of analytical theories of solvation that will be tested by the simulation results and used to explain measured free energies of activation for electron-transfer reactions; and (3) derivation of simplified dynamical theories for quantum mechanical activated processes. These dynamical theories will be used to interpret and guide current simulation studies, and to suggest new experimental work.

University of California, Irvine Irvine, CA 92717

Department of Chemistry

134. Research in Chemical Kinetics

Rowland, F.S.

\$175,000

Comm. 714-856-6016

This research is directed toward understanding the rates and mechanisms of various chemical reactions, including some of importance in the atmosphere or in the oceans. Thermal and energetic reactions of radioactive T and ³⁸Cl atoms are studied with gaseous substrates. Thermalized ³⁸Cl atoms added to the terminal olefinic position in Sn(CH=CH₂)₄ or As(CH=CH₂)₃ form (CH₂=CH)_xMCH-CH₂³⁸Cl* radicals from which the ³⁸Cl atom is able to escape on a time scale much too rapid for consistency with RRKM intramolecular energy equilibration. Additional experiments on ³⁸Cl reactions with a variety of polyvinyl compounds containing central atoms ranging in mass from silicon to lead are being used to characterize these non-RRKM energy transfer processes more precisely. The reactions of thermal ³⁸Cl atoms with hydrogen-substituted chlorofluorocarbon compounds are used to determine the potential importance of an atmospheric sink of stratospheric Cl atoms. The substrate molecules for these reactions are primarily chosen because of their general suitability as substitutes for the chlorofluorocarbon (CFC) molecules in technological applications. Separation procedures are being developed to provide purified 100 microgram quantities of carbonaceous atmospheric molecules (C₂H₆, C₃H₈, OCS) suitable for ¹⁴C determination with mass spectrometry.

University of California, Los Angeles
Los Angeles, CA 90024

Department of Chemistry and Biochemistry

135. Time-Resolved Laser Studies on the Proton Pump Mechanism of Bacteriorhodopsin

El-Sayed, M.A.

\$130,000

Comm. 213-825-1352

The conversion of solar energy into chemical energy (ATP) by a photosynthetic system in nature, bacteriorhodopsin (bR), involves five main steps: (1) energy deposition, (2) separation of charges accomplished by isomerization, (3) protein relaxation leading to deprotonation of the PSB, (4) proton pumping leading to proton gradients, and (5) electric to chemical energy transformation by conversion of ADP into ATP. These studies deal with steps one to three. The function of the protein during the photocycle has been examined in a systematic (but indirect) study of fluorescent protein molecules (i.e., tryptophan, TRP). The observed intensity polarization and lifetimes of the TRP molecules in bR have been studied using picosecond streak camera fluorescence techniques. The number of different TRP sites is determined and their intensity changes are followed under different perturbations (e.g., temperature and pH changes, removing lipids and metal cations). The observed changes are found to support the notion that the protein relaxation determines the rate of the deprotonation process. In order to obtain the details of the conformation changes, the above studies are now being carried out in bR mutants. In addition, the importance of the membrane surface potential and, in particular, the charges on the lipids, are being examined by studying the cycle and its perturbations for reconstituted bR with different lipids. The location and the importance of metal cations to the protein function is also being studied by determining the binding constants of fluorescent Eu^{3+} ions to deionized bR. The presence of one large binding constant which correlates with the function strongly suggests the presence of one metal cation within the active site.

University of California, Santa Barbara
Santa Barbara, CA 93106

Department of Chemistry

136. Cyclometallated and Cyclometalsilylated Complexes of Transition Elements as Photoredox Sensitizers

Watts, R.J.

\$100,000

Comm. 805-893-2032

This research identifies metal complexes that could have application as photocatalysts in photoconversion processes. Primary emphasis is placed on the preparation and characterization of new organometallic species formed in ortho-metalation processes, including studies of complexes of d^6 metal ions including Ir(III), Rh(III), and Ru(II) as well as d^8 metal ions such as Pt(II), Pd(II), and Au(III). Additional research to explore the preparation and characterization of complexes containing metal-silicon bonds has recently been undertaken. This work is focused on complexes that are structurally similar to the organometallic

species under study and is intended to provide insight into what new photocatalytic properties might be associated with metal-silicon-bonded species in comparison to those that contain metal-carbon bonds. Chemical synthesis is used as a starting point in preparing ligands that are then used to form complexes containing either metal-carbon or metal-silicon bonds. These ligands are generally intended to explore the manner in which particular properties of a metal complex (such as redox potential, photoreactivity, luminescence lifetime, solubility, and so forth) can be modified by the ligand. Once prepared and purified, these species are structurally characterized by a variety of physical techniques, including nuclear magnetic resonance (NMR) and infrared spectroscopies as well as X-ray crystallography. Structural information regarding excited states is sought largely with laser-based spectroscopic techniques including emission, time-resolved emission, and excited-state absorption spectroscopies. After their excited-state properties have been established, these materials are excited in the presence of selected substrates in order to establish their excited-state reactivities. Studies of excited-state electron transfer processes are emphasized because of the importance of these types of reactions in many known photoconversion schemes. In this context, several of the ortho-metalated complexes of Ir(III) that are being studied are among the strongest photoreducing agents presently known.

Clemson University
Clemson, SC 29634-1905

Department of Chemistry

137. Intramolecular Energy- and Electron-Transfer Reactions in Polymetallic Complexes

Petersen, J.D.

\$83,909

Comm. 803-656-5017

Preparation of multimetal complexes for use in excited-state, energy- and electron-transfer reactions has involved the generation of new materials. In the case of energy-transfer processes previous work using $[(\text{bpy})_2\text{Ru(II)L}]\text{Rh(III)(PPh}_3)_2\text{H}_2(\text{PF}_6)_3$, where L is a bidentate aromatic azine such as 2,2'-bipyrimidine, resulted in luminescent (luminescent and photoactive) behavior. The threshold for photochemical H_2 production was $2.3\mu\text{m}^{-1}$ irradiation caused by the energy of the Rh(III)-based excited state responsible for this photochemistry. As a consequence, Co(III) homologs have been prepared with a tridentate bridging ligand. Preliminary studies on the photochemistry of $[(\text{NC})_3\text{Fe(II)(tpp)Co(III)(PPh}_3)_2\text{H}_2]$ and $[(\text{tpy})\text{Ru(II)(tpp)Co(III)(PPh}_3)_2\text{H}_2(\text{PF}_6)_3]$, where $\text{tpp} = 2,3,5,6\text{-tetrakis(2-pyridyl)pyrazine}$ and $\text{tpy} = 2,2':6',2''\text{-terpyridine}$, display photoproduction of H_2 at an irradiation threshold of $1.8\mu\text{m}^{-1}$. These latter systems are not as thermally stable as the Ru/Rh systems studied previously. In excited-state, electron-transfer chemistry, highly absorbing Ru(II) azine complexes are to serve as light antennas, viologens or similar organic molecules as electron acceptors bound to one remote metal center, and a cyanoferrate(II) bound to the antenna as an electron donor. Preliminary studies developing spacers between the antenna and electron acceptor, have resulted in the formation of a series of copper(II)

metallopolymer systems. One of these complexes, $[\text{Cu}(\text{H}_2\text{O})_2(\mu\text{-bpm})\text{Cu}(\text{H}_2\text{O})_2(\mu\text{-(OH)}_2)]_x^{(2x)^+}$ has magnetic interactions that are large across both the bpm and $\mu\text{-(OH)}_2$ bridges and a conductivity that is five orders of magnitude greater than the monomer system.

University of Colorado Boulder, CO 80309

Department of Chemistry and Biochemistry

138. Reaction Kinetics and Product Distribution in Photoelectrochemical Cells

Koval, C.A. **\$108,000**
Comm. 303-492-5564

Two fundamental processes associated with photoelectrochemical solar energy conversion are being investigated. First, capture of nonthermalized or "hot" electrons by solution redox species has the potential to increase the efficiencies or to alter the product distribution in liquid junction solar cells. The first distinct product of a hot carrier redox reaction at the p-InP/CH₃CN interface using a Cu(II,I) complex ion has been observed. This system is limited with respect to further exploration of hot carriers; therefore, additional redox systems and experimental techniques that will allow exploration of the phenomenon in greater detail are being developed. If successful, this methodology will be extended to other semiconductor-solution interfaces. The second process under investigation is the kinetics and mechanism of majority carrier charge transfer to solution redox species. Of particular interest is the mechanism for couples with reduction potentials in the bandgap of the semiconductor, i.e., those of greatest importance for photoelectrolysis. These studies utilize the nearly ideal properties of two-dimensional semiconducting materials such as WSe₂ in conjunction with an electrochemical minicell that has been developed. Key aspects of these mechanistic studies are rates measured over extended concentration ranges of redox species and temperature dependence of the reaction rate.

Columbia University New York, NY 10027

Department of Chemistry

139. Theoretical Studies of Photoactive Molecular Systems: Electron Transfer, Energy Transport, and Optical Spectroscopy

Friesner, R.A. **\$110,000**
Comm. 212-854-2202 **(15 months)**

This project describes the development and application of novel theoretical methods to the microscopic calculation of electron transfer, energy transport, and optical spectra of molecular systems of importance in solar photochemistry. The theoretical methods include a new algorithm for *ab initio* electronic structure calculations, a semiclassical surface hopping approach to hot electron dynamics, efficient techniques for diffusive energy and charge transport simulations, numerical methods for determining the optical spectra of large tight binding and one-electron pseudopotential Hamiltonians, and a strategy for solving

the Redfield equations for a large number of system levels. These methods will be applied to the following specific problems: (1) calculation of electron-transfer matrix elements of rigid, bridged donor-acceptor molecules; (2) simulation of the optical spectra of semiconductor particles; (3) determination of the survival probability of excitation diffusing on a polymer with traps, and the relationship of this process to the polymer geometry; (4) electrochemical simulations in complicated geometries; (5) simulation of hot electron dynamics at the semiconductor/liquid interface; and (6) fundamental investigation of the effects of strong electronic coupling on energy and electron transfer, in the context of recent experimental studies of energy transfer in the photosynthetic reaction center and electron transfer mediated by DNA.

140. Single-Collision Studies of Hot Atom Energy Transfer and Chemical Reaction

Valentini, J.J.
Comm. 212-854-7590

This research project focuses on studies of the dynamics of chemical reactions and energy transfer collisions involving reactants or products with hyperthermal energies. Most of the work is experimental, but there is a significant effort in computational modeling of the experimental results. Recent work has focused on the reactions and energy transfer collisions of H atoms with alkanes. The reaction cross sections and product quantum state distributions for the reactions $\text{H} + \text{CD}_4 \rightarrow \text{HD} + \text{CD}_3$, $\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{H}_2 + \text{C}_2\text{H}_5$, and $\text{H} + \text{C}_3\text{H}_8 \rightarrow \text{H}_2 + \text{C}_3\text{H}_7$ have recently been determined at a collision energy of 1.6 eV. Quasi-classical trajectory calculation computer codes are now being developed to model the results of the experiments. The experimental results indicate that the diatomic product is quite cold internally, with an anomalous positive correlation between product vibrational excitation and product rotational excitation. Most of the available energy must be in translation or internal excitation of the alkyl radical. A determination of the energy distributions of the alkyl radical fragments will be made via direct observation of them with coherent anti-Stokes Raman spectroscopy (CARS). The spectroscopic database necessary for this use of CARS is being built up by measurement of the state distributions of the alkyl radical fragments of the photodissociation of alkyl iodides, and a CARS study of CH₃ and CD₃ from CH₃I(CD₃I) photolysis is under way.

Department of Electrical Engineering and Applied Physics

141. Photogenerated Carrier-Induced Reactions on Semiconductor Surfaces

Osgood, R.M., Jr. **\$50,000**
Comm. 212-854-4462

The effect of uv illumination on the chemical reactions on semiconductor surfaces, under ultrahigh vacuum (UHV) conditions is under study. Illumination of a molecular chlorine-covered GaAs(110) surface at 85 K with 193-nm radiation led to the desorption of Cl-atoms as well as the formation of AsCl₃ and Ga, which desorbed at 180 K and Ga desorbing at 210 K, respectively. Illumination with 351-nm excimer-laser radiation caused Cl-atom ejection at a lower rate and resulted in smaller amounts of arsenic chloride formed on the surface. No new species were observed when the surface was irradiated with a 535-nm

laser. It is suggested that the surface reaction is initiated by dissociation of adsorbed molecular chlorine which is mediated either by charge transfer between adjacent molecules or by attachment of photoemitted electrons upon 193-nm irradiation. The laser-induced dissociation of other chlorine containing molecules such as Cl_2CO and Cl_2SO will be studied. Finally, the construction of a second UHV system for the study of laser-induced dissociation of metal alkyls and methyl halides on GaAs surfaces has been completed. This system will incorporate total-internal-reflection Fourier-transform ir spectroscopy to follow reaction intermediates, in addition to a mass spectrometer, low-energy-electron diffraction and Auger-electron spectroscopy.

**Dartmouth College
Hanover, NH 03755**

Department of Chemistry

142. Photoexcited Charge Pair Escape and Recombination

Braun, C.L. **\$75,000**
Comm. 603-646-2500

The escape and recombination of charge pairs produced by photoexcitation of organic molecules is studied in solids and liquids. Measurement of transient absorption by electrons is used to resolve the picosecond time scale recombination of the geminate charge pairs formed by laser photoionization of solute molecules in liquid hexane. The observed decay kinetics are studied as a function of temperature and photon energy and are found to be consistent with a detailed theory of Coulomb-field-dominated, diffusive recombination of geminate electron-cation pairs. The kinetic measurements give direct information about the initial distribution of electron-cation radii in the thermalized charge pairs. In solid-state electron donor-acceptor materials comprised of organic molecules, the escape and recombination mechanism is apparently quite different. Photocurrent that arises from single-photon excitation in the charge-transfer absorption band of the 1:1 mixed crystal, phenanthrene:pyromellitic dianhydride rises in less than a few nanoseconds. Thus, the observed photocurrent does not originate from dissociation of the relaxed charge-transfer (CT) excited state that is observed by fluorescence to have a lifetime of 12 nanoseconds. It is possible that the fast-rising photocurrent originates from reorientation of the CT exciton in an applied electric field. Attempts to assess that possibility led to the discovery that the reorientation of dipolar excited states (in solution) can be followed by time-resolved conductivity measurements. That technique may be generally useful for quantifying the subnanometer motion of charge pairs. In order to understand factors that limit efficient charge-pair separation in such charge-transfer solids, various donor-acceptor geometries are being explored.

**University of Houston
Houston, TX 77204-5641**

Department of Chemistry

143. Charge Separation in Photoredox Reactions

Kevan, L. **\$125,000**
Comm. 713-749-3732

This research is directed toward an improved molecular understanding of the structural aspects controlling charge separation in photoredox reactions in organized molecular assemblies such as micelles and vesicles. Photoionization of chlorophyll, alkylporphyrins, alkylphenothiazines, and derivatives and photoreduction of alkylmethylviologens in frozen solutions of vesicles, micelles, and reverse micelles to produce net charge separation are being studied by electron spin resonance and electron spin echo modulation spectroscopy. These instrumental techniques make possible the detection of the local environment of the photoproduced radical cation with respect to the vesicular structure. Current emphasis is on location control of electron donors and electron acceptors relative to the assembly interface by attachment of variable length alkyl chains and modification of the interface with cosurfactants. In the last year a newly synthesized series of alkylphenothiazines has been studied. Changes in location can be monitored by electron spin echo modulation spectroscopy. The photoionization efficiency is being assessed by electron spin resonance intensities. This work is leading to the general objective of molecular structural control of the photoinduced charge separation efficiency.

**Marquette University
Milwaukee, WI 53233**

Department of Chemistry

144. Resonance Raman and Photophysical Studies of Transition Metal Complexes in Solution and Entrapped in Zeolites

Kincaid, J.R. **\$83,000**
Comm. 414-288-3539

The long term goal of the project involves the study of the photochemical and photophysical properties of transition metal complexes of nitrogen heterocycles (especially polypyridines and phthalocyanines). Current interest is focused on the effect of ligand asymmetry; either inherent or environmentally induced. Resonance Raman, time-resolved resonance Raman, and lifetime measurements are used to investigate the structure and dynamics of ground and $^3\text{MLCT}$ excited states of asymmetric bipyridine complexes of ruthenium(II) under various conditions, i.e., dissolved in various solvents or trapped in the supercages of Y-zeolite. Specifically, the effects of steric restrictions and the high electrostatic charge of the cages on both the ground and excited states of various bis-heteroleptic complexes are under investigation. With respect to inherently asymmetric complexes, initial interest has been focused on simple, readily available ligands such as pyridyl-pyrazine and 4-monomethyl-2,2'-bipyridine.

**Massachusetts Institute of Technology
Cambridge, MA 02139**

Department of Chemistry

- 145. Photochemical Approaches to Conversion of Light to Electricity or Fuel**
Wrighton, M.S. **\$325,000**
Comm. 617-253-1597 **(16 months)**

The objective of this research project is to design, synthesize, characterize, and demonstrate interfacial systems for the conversion of light to electricity or chemical fuel. Areas to be investigated include (1) semiconductor surface chemistry (to improve efficiency and durability of photoconversion systems); (2) multicomponent redox molecules (to mimic the essential functions of natural photosynthesis of light absorption, charge separation, and charge transport); and (3) surface modification reagents (to tailor the properties of electrodes used in photoconversion processes). Unique surface chemistry of semiconductors has led to efficient photoconversion devices. Preliminary results show promising leads in molecular approaches to photoconversion which theoretically will be no less efficient than semiconductor-based devices. Molecular systems under study include donor-chromophore-acceptor molecules such as covalently linked ferrocene-porphyrin-viologen systems capable of being linked to electrode surfaces.

**University of Massachusetts at Boston
Boston, MA 02125**

Department of Chemistry

- 146. Magnetic Resonance Studies of Photoinduced Electron Transfer Reactions**
van Willigen, H. **\$94,000**
Comm. 617-287-6147

Time-resolved electron paramagnetic resonance (EPR) techniques are used in the study of the factors that affect excited-state electron transfer reactions. During the past year the investigations have been concerned mainly with the application of Fourier Transform (FT) EPR. With this spectroscopic technique the formation and decay of pulsed-laser generated electron transfer products can be monitored with nanosecond time resolution and high sensitivity. The measurements give the rate constants of forward- and back-electron transfer reactions. Moreover, FT-EPR spectra convey information on the characteristics of transient intermediates involved in the reaction. Of particular interest is that the method can be used to study the formation and decay of radical pair intermediates. Measurements have been performed on: (1) zinc tetraphenylporphyrin (ZnTPP) /benzoquinone (BQ) (or duroquinone, DQ) in homogeneous solution and in micellar media; (2) tetrasulfonated ZnTPP (ZnTPPS)/BQ in water-ethanol mixtures; and (3) ZnTPPS /DQ in micellar solution. This project will examine the role the solvent medium plays in the electron transfer process, and to what extent electrostatic interactions between donor and acceptor molecules affect the characteristics of the transient radical pairs and the efficiency of the excited-state electron transfer process.

**University of Minnesota
Minneapolis, MN 55455**

Department of Chemistry

- 147. The Contribution of Electronically Excited States to the Radiation Chemistry of Organic Systems**
Lipsky, S. **\$95,966**
Comm. 612-624-9581

Photophysical properties of organic molecules are being studied that have relevance in determining their behavior when subjected to high-energy radiation. Because ion pairs are important precursors of chemical damage in irradiated liquids, recent studies have concentrated on their properties. The ion pairs are generated by photoionization, and their decay is observed by (1) recombination (to give fluorescence) and (2) "escape" (to give photocurrent). Observations are made as functions of photon energy, nature of the liquid, and strength of externally applied electric and magnetic fields. Current work includes (1) measurements of fluorescence spectra and fluorescence quantum yields from recombining geminate positive ions and electrons in neat hydrocarbon liquids as a function of excitation energy (this study gives information on the nature of the intermediate electronic states that are generated during the annihilation process); (2) measurement of the effect of a magnetic field on geminate ion recombination fluorescence induced by pulsed vacuum ultraviolet excitation of neat hydrocarbon glasses (the magnitude of this effect provides information on loss of spin coherence during the time interval of recombination); and (3) measurement of the electric field dependence of the photocurrent spectra of anthracene in hydrocarbon solutions. From these data are developed theoretical models of the nature of the ionizing transition in liquids.

**National Institute of Standards and
Technology, Gaithersburg
Gaithersburg, MD 20899**

Chemical Kinetics Division

- 148. Pulse Radiolytic Studies of Electron Transfer Processes and Applications to Solar Photochemistry**
Neta, P. **\$195,000**
Comm. 301-975-5635

The pulse radiolysis technique is applied to the study of electron transfer processes in a variety of chemical systems. Reactive intermediates are produced in solution by electron pulse irradiation and the kinetics of their reactions are followed by time-resolved absorption spectrophotometry. These studies are concerned with mechanisms, kinetics, and thermodynamics of reactions of organic and inorganic radicals and unstable oxidation states, in aqueous and nonaqueous solutions. For studies of aqueous solutions, emphasis is focused on the unique ability of pulse radiolysis to provide absolute rate constants for reactions of many inorganic radicals and organic peroxy radicals, species that are key intermediates in many chemical processes. Current measurements on the temperature effects on rate constants for reactions of

these radicals provide further insight into their mechanisms. A special emphasis of this work is the study of electron transfer reactions of metalloporphyrins that may be applicable to solar energy conversion systems. These include one-electron reduction and oxidation, on the porphyrin ring versus that on the metal center, and the structural and medium effects that may influence them. Reactions of porphyrin radical anions and cations with colloidal catalysts that may lead to solar energy conversion and storage (e.g., to decomposition of water to hydrogen and oxygen) are also studied.

**University of North Carolina at
Chapel Hill
Chapel Hill, NC 27599-3290**

Department of Chemistry

- 149. Excited-State Processes in Transition
Metal Complexes. Applications to Redox
Splitting in Soluble Polymers**
Meyer, T.J. **\$125,000**
Comm. 919-962-6319

Polyppyridyl complexes of certain transition metal ions are being investigated for applications in energy conversion processes at the molecular level. Based on the photochemical and photophysical properties of these complexes, patterns of behavior are emerging that allow stabilities and lifetimes to be predicted. By utilizing transient laser techniques and emission and resonance Raman spectroscopies, the roles of electronic structure, molecular vibrations, and the medium on properties and lifetimes are being investigated systematically. Synthetic methods have been developed for attaching derivatives of these complexes to soluble polymers along with organic fragments which can act as electron or energy transfer donors or acceptors. Studies on these complex arrays show that polymers can be designed in which photoinduced electron or energy transfer events can be initiated and controlled on single polymeric strands. Polymeric systems are currently being designed that will mimic the light-harvesting, electron transfer capabilities of the reaction center of photosynthesis, and provide a basis for exploring long-range electron or energy transfer.

**University of North Carolina at Char-
lotte
Charlotte, NC 28223**

Department of Chemistry

- 150. Oligomer and Mixed-Metal Compounds:
Potential Multielectron Transfer Agents**
Rillema, D.P. **\$96,000**
Comm. 704-547-4445

The design and synthesis of potential solar energy photocatalysts is the focus of the investigation. New classes of photoactive complexes have been isolated. These are a copper(I) complex based on a new phenanthroline-like ligand, biphenyl complexes of platinum(II), and a bimetallic complex of ruthenium(II) and rhenium(I). The

copper(I) complex contained the ligand 1,2-bis(9-methyl-1,10-phenanthrolyl-2-yl)ethane and luminesced in fluid solution at room temperature. The platinum(II) biphenyl complexes contained the ancillary ligands 1,10-phenanthroline, 4,4'-dimethyl-2,2'-bipyridine, 2,2'-bipyridine and 2,2'-bipyrimidine. The luminescence of the platinum(II) complexes was dependent upon the temperature, the solvent, and the excitation wavelength. Excitation at 436 nm in 2-methyltetrahydrofuran resulted in the appearance of a broad emission identified as ³MLCT based; excitation at 355 nm in the same solvent resulted in a sharp emission profile containing fine structure which was attributed to ³LC emission. The bimetallic complex containing ruthenium(II) and rhenium(I) bridged by 1,2-bis(4-methyl-2,2'-bipyridyl-4-yl)ethane luminesced at 540 and 610 nm. The luminescence at 610 nm was derived from the ruthenium(II) component and the one at 540 nm was derived from the rhenium(I) component. Comparison of luminescence intensities to those of the monometallic precursors leads to the conclusion that energy transfer occurs from the ³MLCT state of the rhenium(I) component to the ³MLCT state of the ruthenium(II) component. Only radiative energy transfer can be ruled out as a possible mechanism for the process.

**Northwestern University
Evanston, IL 60208-3113**

Department of Chemistry

- 151. Dynamic Structural Effects and Ultrafast
Bimolecular Kinetics in Photoinduced
Charge Transfer Reactions**
Hupp, J.T. **\$180,000**
Comm. 708-491-3504 **(18 months)**

This project involves: (1) time-dependent scattering studies of vibrational structural changes accompanying chemically important photoredox processes; (2) collaborative studies of femtosecond charge-transfer kinetics in fully vibrationally characterized systems; and (3) studies of ultrafast bimolecular redox quenching of very short-lived excited states, based on greatly accelerated diffusional transport in a supercritical medium. A significant accomplishment during the current year has been the elucidation of the mechanism by which the external solvent modulates the internal vibrational reorganization energetics in a prototypical charge-transfer system, Ru(2,2'-bipyridine)₂(CN)₂⁰. Ground- and excited-state Raman studies reveal that the controlling factor is the way in which state-specific hydrogen-bonding from the solvent influences the chromophoric energy gap and therefore the extent of ground-state/excited-state mixing. The results are important, in part, because they provide the first detailed microscopic demonstration of how key internal modes for a molecular photo-redox system can be coupled to (and controlled by) the external environment.

**Ohio State University
 Columbus, OH 43210**

Department of Chemistry

152. Photoinduced Electron Transfer Reactions in Zeolite Cages

Dutta, P.K. **\$80,000**
 Comm. 614-292-4532

Photochemistry in constrained heterogeneous medium offers opportunities for stabilizing photodriven chemical products that cannot be readily done in homogeneous solution. This project will exploit the architecture of the cavities of zeolites and interlayers of anionic clays as sites for photosensitizer molecules. In particular, the emphasis is on $\text{Ru}(\text{bpy})_3^{2+}$ in supercages of zeolite Y and ZnTPPS dispersed in a lipid-like environment in the interlayers of an anionic clay material, $\text{LiAl}_2(\text{OH})_6^+$. In both these cases, visible photoexcitation leads to electron transfer from the trapped sensitizer to electron acceptors such as viologens in solution. The back electron transfer is considerably slowed down, thereby allowing for accumulation of reduced viologen in solution under steady-state illumination. Transient spectroscopic experiments are in progress to determine the kinetics of the process and determine the factors that lead to the slowing down of the back reaction. The rates also appear to be influenced by the charge of the viologen and the length of its hydrophobic component. The role of the exchangeable cations in the zeolite matrix that are responsible for charge neutralization upon electron transfer is being examined. Various spectroscopic techniques, including steady-state and time-resolved absorption, emission, Raman, and lifetime measurements are being used to probe the structure of the ground and excited states of the photosensitizer in the zeolite cages.

**Oregon Graduate Institute of Science
 and Technology
 Beaverton, OR 97006**

Department of Chemical and Biological Sciences

153. Fundamental Studies in Oxidation-Reduction in Relation to Water Photolysis
 Hurst, J.K. **\$105,000**
 Comm. 503-690-1073

This project aims to improve the conceptual understanding of the influence of microphase separation and compartmentation upon oxidation-reduction processes. Three goals are: (1) to use interfaces to promote charge separation and increase lifetimes of the initial redox products, (2) to identify mechanisms of transmembrane redox across bilayer membranes, and (3) to develop regenerative cycles for water photolysis. Concerning goal 1, photo-induced charge separation in totally artificial self-assembling photoredox systems has been achieved, the quantum efficiencies of which approach that of natural photosynthesis; lifetimes of the immediate products, which are phase separated, exceed 10 ms. With respect to goal 2, viologen transmembrane redox mechanisms have been unambiguously identified, which involve either "flip-flop" diffusion or long-range electron tunneling between

reactants bound at the opposite membrane interfaces. Either of the pathways can be selected by appropriate derivatization of the redox dopant ion. Goal 3 entails determination of water oxidation mechanisms by a series of dimeric ruthenium μ -oxo ions. These studies have involved the use of ^{18}O isotopic tracers, as well as various structural and kinetic methods. Current efforts are directed at incorporating these components into integrated systems for water photolysis and developing photogated switchable conducting membranes exhibiting rectification.

**Pennsylvania State University, University Park
 University Park, PA 16802**

Department of Chemistry

154. The Gaseous Free-Radical and Ion Chemistry of Silanes, Germanes, and Phosphines
 Lampe, F.W. **\$75,000**
 Comm. 814-865-3029

This research project includes four activities. The first activity will develop an understanding of the chemical kinetics and mechanisms involved in the gas-phase photochemical decompositions of silane, germane, and phosphine systems. Emphasis is on the reactions of silylene, silyl, germylene, and germyl radicals with silane, germane, and phosphine, as well as with each other and with various inorganic and organic substrates. The second activity involves (1) elucidation of the ion-molecule reactions characteristic of ionized silane, germane, and phosphine, and silane-germane, silane-carbon monoxide, germane-phosphine, germane-hydrogen, and germane-water mixtures and (2) measurement of the pertinent rate coefficients and cross sections. Such knowledge is critically important in understanding and modeling the immensely complex chemistry involved in electrical discharge and plasma chemistry. The third activity involves (1) acquisition of kinetic and thermochemical data, particularly in regard to silanes, germanes, and phosphines and (2) advancement of understanding of the kinetics and kinematics of elementary chemical reactions in general. The fourth activity will investigate the formation of thin films of amorphous silicon (a-Si:H) produced by the low-intensity γ -ray irradiation of silane admixed with noble gases.

155. Experimental and Computational Studies of Polar Solvation
 Maroncelli, M. **\$90,000**
 Comm. 814-865-0898

The focus of this project is on understanding how polar solvents influence electron and other charge transfer reactions in solution. Of special interest are dynamical aspects of the solvation process and the role that such dynamics play in determining charge transfer rates. A number of recent theories have predicted a proportionality between the rate of electron transfer and solvent reorganization rates. Time-resolved fluorescence studies on simple intramolecular charge transfer reactions are used to explore this connection. An important part of the work currently in

progress also involves obtaining a prerequisite understanding of the dynamics of solvation in nonreactive systems. Results obtained to date indicate that the time scales of solvation in polar liquids are poorly predicted by simple continuum models of solvation. But it is just such models that have been used to theoretically study the connection between solvation and electron transfer. In order to build a more adequate understanding of charge transfer in solution it is first necessary to better understand and model the dynamics of solvation in simple, nonreactive situations. Time-resolved experiments and molecular dynamics computer simulations are being used to probe the dynamics of solvation in a variety of solvents and solvent mixtures. The goal of this work is to develop and test simple models of the static and dynamic aspects of polar solvation of relevance to the solvent-reaction coupling.

University of Pittsburgh Pittsburgh, PA 15260

Department of Chemistry

156. Time-Resolved Studies of Carrier Recombination at the Semiconductor-Electrolyte Interface

Waldeck, D.H. **\$90,000**
Comm. 412-624-8430

This research program addresses the kinetics of charge carrier relaxation at the semiconductor-electrolyte interface. Because of the complexity of this interface a variety of tools, both optical and electrical, are used to characterize the structural properties in conjunction with the kinetic studies. The main emphasis of the research is on the relaxation of charge carriers at a semiconductor surface in contact with an inert electrolyte. The fundamental processes in this relaxation are characteristic of the processes that occur in heterogeneous redox chemistry and a second aspect of this project is to study heterogeneous redox chemistry. The initial studies have focused on the carrier relaxation in n-type CdSe [a direct gap material (1.75 eV)]. Preliminary studies have been performed under high injection conditions under which the band bending is minimized. A simple diffusion model for the hole dynamics is not appropriate for the material under these conditions. Computer simulation studies in conjunction with the experimental studies indicate that a finite lifetime of surface state traps could explain these observations. The importance of interfacial traps to the carrier relaxation is being explored by chemical derivatization. In particular ClSi(Me)₂X reagents are being used to bind a monolayer of Si(Me)₂X to the surface (X = CH₃, C₆H₆, OCH₃...). The derivatization of the surface has been verified by secondary ion mass spectrometry and changes in the time resolved fluorescence. Comparison of these observations with models of carrier relaxation are in progress.

Portland State University Portland, OR 97207-0751

Department of Chemistry

157. Asymmetric, Interfacially-Polymerized Porphyrin Films for Artificial Photosynthesis

Wamser, C.C. **\$90,000**
Comm. 503-464-3811

This project involves the synthesis and characterization of novel thin-film polymer membranes made from porphyrins. The polymer films are prepared by interfacial polymerization of a pair of reactive monomers, for example from tetra(p-aminophenyl)porphyrin (TAPP) in DMSO with tetra(p-chlorocarbonylphenyl)porphyrin (TCCPP) in ethyl acetate, or from tetra(p-hydroxyphenyl) porphyrin (THPP) in aqueous base with TCCPP in chloroform, or from various aliphatic diamines in water with TCCPP in chloroform. Typical film thicknesses are in the range of 0.01 to 10 μm depending on the particular monomers and reaction conditions. The films display a unique chemical asymmetry, in the sense that opposite surfaces of the films show distinctive differences in the concentration and type of functional groups that are present. When placed between semitransparent electrodes and irradiated with either steady-state broad-band light or a pulsed laser, these films develop directional photopotentials. The directional photopotentials are considered to be a manifestation of the chemical asymmetry of these interfacial films, that is, photoinduced charge separation involves electron transfer in the direction that corresponds to the predicted trends of oxidation and reduction potentials of the various porphyrins within the polymer film. The major goals of the current research are (1) characterization of the structural asymmetry of the films and its correlation with the photoactivity and (2) optimization and control of the asymmetric photoactivity.

Princeton University Princeton, NJ 08544-1009

Department of Chemistry

158. Surface Chemistry at Semiconductor-Electrolyte Interfaces

Bocarsly, A.B. **\$88,000**
Comm. 609-258-3888

This study involves the deliberate chemical modification of II-VI semiconductor-based photoelectrochemical cell interfaces in order to arrest photodecomposition processes while enhancing the efficiency of light to electricity conversion. Recent work has focused on the photodeposition of platinum metal from solution and the surface chemistry of n-CdX (X = S or Se) photoelectrodes in a cyanometalate-containing electrolyte. Illumination of a II-VI interface in a Fe(CN)₆^{4-/3-} containing electrolyte is found to produce a layer of cadmium metalocyanide on the electrode surface. This overlayer has alkali cation exchange properties. It is found that the redox properties (energetic and kinetic) of the overlayer can be controlled by intercalation of appropriate cations. Thus, the semiconductor/overlayer interfacial properties can be maximized

with respect to both the band structure of the semiconductor and the thermodynamics of the electrolyte. Consideration of this type of interfacial microstructure has led to the development of an n-CdSe based cell (ferrocyanide electrolyte) with good stability and monochromatic light energy to electricity conversion efficiencies (488 nm) of 30 to 40%. Further improvement in the observed photovoltage can be obtained by substitution of $\text{Mo}(\text{CN})_8^{4-}$ for $\text{Fe}(\text{CN})_6^{4-}$ in the interfacial layer. Once the cyanometalate overlayer has been formed and stabilized, substitution of an optically transparent electrolyte, such as CN^- or ascorbate for the cyanometalate electrolyte, produces an electrolyte suitable for conversion of white light to electricity. To date, electricity conversion efficiencies of 6% have been observed for solar irradiation using an ascorbate electrolyte, while a CN^- electrolyte produces a current doubling effect yielding a limiting quantum yield of 1.8. In a separate set of experiments, it has been demonstrated that a wide variety of surfaces can be metalized with good spatial resolution by the photochemical reduction of PtCl_6^{2-} in the presence of alcohol. This chemistry can be employed to directly convert optical energy to chemical energy or in conjunction with the semiconductor photoelectrochemistry indicated above to generate semiconductor-metal junctions.

159. Resonance Raman Spectroscopy of Metalloporphyrins and Photoreaction Centers

Spiro, T.G. \$110,000
Comm. 609-258-3907

The photochemistry of metalloporphyrins is being explored with a view toward developing new photoenergy transfer catalysts. Porphyrin cation and anion radicals, the primary products of electron-transfer reactions, have been studied by resonance Raman spectroscopy. These studies have been supported by semiempirical molecular orbital calculations. The calculations strikingly support the experimental evidence for a bond-alternant distortion of the porphyrin skeleton in radical cations having a_{1u} character. These studies are being extended to porphyrin excited states using time-resolved Raman techniques. The spectrum of triplet zinc tetraphenylporphyrin has been obtained, and assigned with the aid of isotopic data. The spectrum provides evidence for symmetry lowering via a Jahn-Teller effect. Modified porphyrins have been synthesized in which donor and acceptor substituents are expected to stabilize charge transfer excited states having transiently reduced or oxidized central metal ions. Redox chemistry of these transient states, particularly hydrogen and oxygen atom transfer reactions, are being developed.

University of Rochester
Rochester, NY 14627

Department of Chemistry

160. Photochemistry and Charge Transfer Chemistry of Dithiolate Complexes of the Platinum Group Elements

Eisenberg, R. \$105,000
Comm. 716-275-5573

This project focuses on the synthesis, characterization, and photochemistry of new square planar complexes of

the platinum group elements which luminesce in fluid solution. Mononuclear complexes of this type are extremely rare, but would be useful as photocatalysts because of their inherent coordinative unsaturation. Current efforts have concentrated on Pt(II) complexes of the formula $\text{Pt}(\text{N}-\text{N})(\text{S}-\text{S})$ where N-N is a diamine, bipyridine, or o-phenanthroline derivative and S-S is a 1,1- or 1,2-dithiolate ligand. The complexes are prepared from the corresponding $\text{PtCl}_2(\text{N}-\text{N})$ species and an alkali metal salt of the dithiolate. The absorption spectra of these systems exhibit an intense band at 450 to 490 nm which is highly solvatochromic and assigned as a charge transfer transition. The emission spectra for the 1,1-dithiolate systems in fluid solution are broad and asymmetric. At low temperature, evidence of multiple emitting states is obtained with the emergence of new emission bands ascribable to a diamine $\pi\pi^*$ state. Both lifetime and quantum yield measurements as functions of temperature have been performed for several of the complexes. The emitting state in these complexes, while not unambiguously established, appears to be a charge transfer state involving the metal and the dithiolate ligand. The ecda complexes (ecda = ethyl-2-cyano-3,3-dithioacrylate) have been studied most extensively because of their greater solubility. Electron transfer quenching of the emission of some ecda complexes has been observed to follow good Stern-Volmer kinetics using either a dialkylaniline donor or a nitrobenzaldehyde acceptor.

161. Ultrafast Optical Studies of Surface Reaction Processes at Semiconductor Interfaces

Miller, R.J.D. \$160,000
Comm. 716-275-4079

Electron transfer is the primary photophysical process in solar energy conversion, lying at the heart of photosynthesis and almost all solar cells. Fundamental differences exist between electron transfer involving exclusively molecular states and electron transfer processes at surfaces that remain to be resolved. At a surface, the electronic coupling is occurring across an abrupt phase discontinuity. The very nature of the phase boundary dictates that the electronic coupling involves states derived from localized molecular potentials for the adsorbate and extended states derived from the periodic potential of the solid state. The highly delocalized nature of the electronic states in the solid state and the enormous number of states that can couple to the reactive coordinate for electron transfer introduce significant differences in the problem of electron transfer at surfaces relative to homogeneous electron transfer. The impurities in the surface structure create surface states that are also involved in the overall electron transfer mechanism. The main focus of this research is to use novel time domain spectroscopies to address directly the dynamics of interfacial electron transfer at semiconductor surfaces, which are related to the degree of electronic coupling across the interface and the solid-state density of states. The studies follow both the acceleration of the photogenerated charge carriers in the surface space charge region and the carrier depletion at the surface region. These studies will provide a complete mapping of the electron trajectory as it crosses the interface. This information is important to a detailed understanding of surface photochemistry as well as a direct determination of the ratio of hot electron versus thermalized electron transfer. This latter information will

determine the maximum energy conversion efficiency possible for liquid junction solar cells.

162. Photoinduced Electron Transfer Processes in Homogeneous and Microheterogeneous Solutions

Whitten, D.G. \$130,000
Comm. 716-275-4231

These investigations are focused on light-induced redox reactions in solution that can lead to efficient and potentially useful net chemical reactions. Most of these processes are initiated by single-electron transfer quenching of an excited state followed by subsequent steps often involving cooperative reactions between ion radicals formed in the quenching step. Recent efforts have used chiefly visible light-absorbing acceptors; in most cases the electron donors studied do not absorb light in the near ultraviolet or visible and would thus have no long wavelength photochemistry in the absence of the acceptor. The donors typically have at least one heteroatom functionality (amine, alcohol, thiol, thioether, ether) which is the site of the single-electron transfer oxidation by the excited acceptor. Suitable location of a second heteroatom can result in the selective labilization of a specific C-C bond in the molecule so that the net reaction is a two-electron oxidative carbon-carbon bond cleavage process in the donor concurrent with a net two-electron reduction of the acceptor. Frequently the sites of initial single-electron transfer oxidation of the donor and of permanent two-electron redox are quite different. These studies are furnishing a paradigm for understanding this reactivity. These investigations are leading to an understanding of solvent effects, stereochemical requirements, the role of acceptor and donor structure, and reaction energetics. It has been found that relatively low energy light can promote the clean and efficient cleavage of strong carbon-carbon bonds and that initial single-electron transfer at one site in an organic donor can culminate in clean two-electron oxidation at another site several atoms removed from the initial point of attack.

**Rutgers University
Piscataway, NJ 08855-0939**

Department of Chemistry

163. Long-Range Intramolecular Electron Transfer Across Synthetic Polypeptides

Isied, S.S. \$105,000
Comm. 201-932-3764

This research focuses on demonstrating long-range intramolecular electron transfer across rigid polypeptide ligands. Metal ion donors of the substituted ruthenium polypyridine type are covalently attached at the N terminal of oligoproline bridging ligands and metal ion acceptor complexes are covalently attached to the O terminal of the oligoproline bridging ligands. Intramolecular electron transfer reactions are studied in these donor/acceptor molecules using pulse radiolysis and flash photolysis techniques. Rapid rates of electron transfer (ca msec time scale) have been observed at distances approaching 30 Å. Extension of this work to even longer distances, ca 40 Å, with polypeptides of more defined secondary structures is

currently in progress to elucidate the role of protein secondary structure mediation in electron transfer pathways.

**University of South Florida
Tampa, FL 33620**

Department of Chemistry

164. Frontier Orbital Symmetry Control of Intermolecular Electron Transfer

Stevens, B. \$84,000
Comm. 813-974-2896

Electron transfer quenching of 9,10-dicyanoanthracene fluorescence by electron donors in polar solvents over the temperature range 273 to 323 K has been analyzed in terms of the finite sink model. In solvents of low viscosity the quenching rate constant k_q is independent of quencher concentration C and equal to the equilibrium statistical rate constant k° for rate-limiting electron transfer. Quenching becomes diffusion-limited at high solvent viscosity and permits independent recovery of the relative diffusion coefficient D , the encounter diameter ρ , and the parameter k° under diffusion-influenced conditions. The dual fluorescence of 4,4'-terphenyl and 9,9'-bianthryl linked electron donor/acceptor systems each exhibit biexponential response functions with apparently unrelated amplitudes and time constants. Longwave and shortwave components, selectively quenched by water and halocarbons respectively, are accompanied by fluor consumption indicative of a chemical quenching process. It is planned to examine fluorescence quenching effects by rubrene endoperoxide which has been shown to form different products from initially oxidized and reduced forms. Time-dependent transient absorption by the naphthalene donor cation following selective pulsed excitation in each absorption band of the tetracyanoethylene EDA complex in polar solvents exhibits no long-lived hyperbolic component characteristic of homogeneous radical-ion recombination, and fast exponential components have the same time constant (with ps resolution) for excitation in each band. Other systems exhibiting dual CT absorption bands in solvents of low polarity are under investigation. The effect of transient (van der Waals) mode symmetry on transformation properties of vibronic surfaces describing electron transfer has been examined for donor/acceptor complexes belonging to C_s and C_{3v} point groups.

**Stanford University
Stanford, CA 94305-5080**

Department of Chemistry

165. Energy Transfer Processes in Solar Energy Conversion

Fayer, M.D. \$200,000
Comm. 415-723-4446

Experimental and theoretical studies are being used to investigate fundamental aspects of processes important to solar photochemistry energy conversion. Two areas being studied are photoinduced electron transfer and electronic excitation transfer. Recently, detailed investigations of the influence of the diffusion of molecules on photoinduced

electron transfer have been conducted. The electron transfer is monitored with time-correlated single photon counting fluorescence measurements. Comparison between experiments and theory, which includes excluded volume effects, shows excellent agreement. These are the first experimental results that can be quantitatively calculated with a detailed theory. Using picosecond pump-probe experiments, data have been taken to study electron back transfer following photoinduced forward transfer in solution. A theory has been developed that includes the role of diffusion. A detailed theory of electronic excitation transport for systems of high concentrations of clustered chromophore systems was derived. Calculations were performed for high concentrations of micelles containing chromophores. The theory includes not only transfer among chromophores on a micelle, but also, transfer from one micelle to another. The theory is being extended to excitation transfer in systems of microphase-separated polymers in which the aggregated chains are tagged with chromophores.

Syracuse University
Syracuse, NY 13244

Department of Chemistry

**166. Photochemical Solar Energy Conversion
Utilizing Semiconductors Localized in
Membrane Mimetic Systems**
Fendler, J.H. **\$125,000**
Comm. 315-443-4146

Size-quantized semiconductor particles, generated at bilayer lipid membrane and monolayer interfaces, are used in artificial photoconverting systems. Cadmium sulfide, zinc sulfide, and their mixtures (with grain sizes between 50 Å and 200 Å) are characterized by absorption spectroscopy, transmission electron microscopy, scanning tunneling microscopy, and scanning electrochemical microscopy. Investigation of size-dependent photoelectron transfer allows the optimization of these systems for photochemical solar energy conversion.

University of Tennessee
Knoxville, TN 37996-1600

Department of Chemistry

**167. Studies of Radiation-Produced Radicals
and Radical Ions**
Williams, T.F. **\$120,000**
Comm. 615-974-3468

The objective is to characterize the structure and reactivity of organic free-radical and radical-ion intermediates generated by irradiation of molecular systems. A particular focus is the study of the radical ions that are generated in the primary chemical processes resulting from the absorption of high-energy radiation, since these charged species play an important role in the mechanisms of both radiation and photochemical effects. Radical cations are formed radiolytically under matrix-isolation conditions by γ -irradiation of solid solutions of the parent compounds in

Freon matrices at low temperatures. Conversely, radiolytic reduction can be accomplished in hydrocarbon and other organic matrices where the positive hole is trapped and the electron can migrate to a solute molecule. Electron spin resonance and electronic absorption spectroscopy are used to characterize these paramagnetic species; measurements of g factors and hyperfine coupling constants are being made on isotopically labeled and diastereomeric radicals to obtain information about molecular geometry and spin density distribution. Specific projects include: (1) structural aspects of novel species, (2) ion-molecule reactions and rearrangements, (3) photochemistry of radical ions, and (4) structure-reactivity relations.

University of Texas at Austin
Austin, TX 78712

Department of Chemistry

**168. Vectorial Electron Transfer in Spatially
Ordered Arrays**
Fox, M.A. **\$175,000**
Comm. 512-471-1811

Mechanisms of photocatalytic oxidation and reduction reactions of organic adsorbates on native and chemically modified semiconductor surfaces can be altered by modifying the chemical bonds on the surfaces. Organometallic coordination polymers and N-alkylated nicotinamide derivatives are being tested as relays for multiple electron transfer. Electrodes modified for electrocatalytic studies are being prepared by anchoring the specifically designed electrocatalysts by covalent binding, electrosorption, and chemisorption of redox active polymer layers. Spatially controlled monolayer and bilayer coatings can attain electrical rectification in those photoelectrochemical cells. Polymers are being synthesized as vehicles for efficient light collection and vectorial energy migration.

**169. Electron Transfer Reactions in Micro-
porous Solids**
Mallouk, T.E. **\$104,000**
Comm. 512-471-5903

This project uses porous solids, such as aluminosilicate zeolites and clays, and microporous oxide semiconductors, as organizing media for molecular electron transport assemblies, in much the same way as membrane proteins are used in the natural photosynthetic system. In these systems, self-assembly is driven by ion-exchange equilibria, size exclusion effects, and specific adsorption. Attachment of these particles to electrode surfaces, in combination with appropriate light-adsorbing and redox-active molecules, gives electrodes that behave electrochemically as photodiodes. The factors that influence their photocurrent efficiency are currently being studied. The photochemistry of multicomponent donor-sensitizer-acceptor systems organized by zeolites is also being investigated. A particularly promising system of this kind involves the use of a sacrificial donor (EDTA or triethanolamine) with a ruthenium polypyridyl sensitizer adsorbed onto a zeolite/TiO₂ particle containing internally sited methylviologen and platinum. Flash photolysis experiments show the vectorial nature of electron transport in this system, and the quantum efficiency for hydrogen production is relatively high (ca. 30%) at the absorbance

maximum of the sensitizer. Efforts are now being directed toward the preparation of sensitized particles that produce hydrogen photochemically using nonsacrificial (electrochemically reversible) electron donors. Sensitized layered semiconductors such as $K_2Ti_4O_9$ and $K_4Nb_6O_{17}$, which contain metal catalyst particles between layers, are also very interesting in this regard. This project also involves fundamental studies of long distance electron transfer between molecules coadsorbed on oxide and chalcogenide semiconductor particles. The role that tunneling and/or superexchange via delocalized semiconductor orbitals plays in accelerating intermolecular electron transfer rates is being investigated.

**170. Polymers at Liquid-Liquid Interfaces:
Photophysics and Photoredox Chemistry**
Webber, S.E. \$90,000
Comm. 512-471-3633

The project objective is to effect charge separation from excited states of chromophores bound to amphiphilic polymers which are adsorbed at the interface between water and an immiscible organic solvent. It is hoped that the polymer will stabilize adsorption because of multiple site interaction at the interface. Ionic groups on the polymer chain provide a driving force for separation of charged radicals via electrostatic repulsion. The liquid-liquid interface can further partition the radical products and increase the overall quantum yield, in addition to protecting the aromatic cation from attack by water. Two polymer systems have been synthesized and are currently being studied: (1) poly(vinylnaphthalene-*alt*-maleic acid) and (2) poly(styrene-*alt*-maleic acid-*co*-chromophore), where the chromophore is vinylphenanthracene, vinylpyrene, or a substituted vinylanthracene. There are several different aspects to these studies. The surfactant properties of these polymers will be determined. This is conducted primarily by interfacial surface tension measurements and by fluorescence quenching measurements. Both classes of polymers have been shown to be surface active. The efficiency of charge separation upon excited state quenching (usually by means of viologens) will be assessed in homogeneous solution. Present studies are emphasizing the triplet excited state. Spectroscopic methods are being developed to determine the efficiency of these same processes in the presence of a liquid-liquid interface.

**Washington State University
Pullman, WA 99164-4630**

Department of Chemistry

171. Investigations of Charge-Separation Processes in Metal Complexes
Crosby, G.A. \$94,998
Comm. 509-335-5605

Thermal modulation spectroscopy is being used to investigate barriers that separate ligand-localized (LL) triplet states and ligand-ligand charge-transfer (LLCT) states in complexes of zinc and cadmium. The intent is to determine the structural and electronic determinants that define the barriers to this charge separation process. Bis(polypyridine) complexes of platinum(II) are also under investigation at low (helium) temperatures to elucidate the nature of the excited states, particularly the role of

the metal ion in promoting ligand-ligand interactions. Triplet sublevel splittings of both LL and LLCT configurations in zinc complexes and LL configurations in rhodium(III) species are also being measured. The results are being related to theoretical computations to ascertain the degree of participation of the metal orbitals in the excited states. Series of platinum(II) mixed-ligand complexes are being synthesized that contain both polypyridine and aromatic thiolate ligands. X-ray structure determinations are under way and sub-77 K studies of their lifetimes and spectra are being conducted.

**Wayne State University
Detroit, MI 48202**

Department of Chemistry

172. Photoinduced Charge and Energy Transfer Processes in Molecular Aggregates
Endicott, J.F. \$168,104
Comm. 313-577-2607

The major goals of this research project involve the systematic investigation of models that will describe various aspects of the photoinduced transfer of charge or migration of energy between donor and acceptor transition metal complexes. Research involves the design and synthesis of molecular systems to be used as mechanistic probes and the characterization of photochemical transients using very sensitive detection techniques. Work in progress varies from studies of the general problem of electronic coupling in donor-acceptor systems to specific problems relating to the pathways for relaxation of the lowest energy excited state of chromium(III). Considerable electronic coupling of donor and acceptor seems to be an important characteristic of polynuclear transition metal complexes with CN^- bridging groups, with the effects of this coupling being manifested largely in photo-physical, and, to a lesser degree even in ground state spectroscopic and electrochemical behavior. In complexes for which the donor excited state is $(^3CT)Ru(bpy)_2^{2+}$ and the acceptor is a cyano-linked Rh(III) ammine complex, the donor and acceptor centers usually behave reasonably independently. The behavior of these complexes is adequately described by a simple sequence of steps, mostly localized at these centers: (1) light absorption by the donor to produce an FC excited state, (2) vibrational and electronic relaxation within the donor to generate the lowest energy CT excited state, (3) equilibration between the donor and acceptor, and (4) relaxation of the electronically excited system. The behavior of the potential electron transfer systems, with Co(III) or Ru(III) am(m)ine acceptors, is more complex and the rate of regeneration of ground states in the Ru(III) ammine acceptor complexes is so rapid (≤ 25 ps) that discrete electron transfer steps may not be a feature of the relaxation sequence.

Chemical Physics

Aerospace Corporation
Los Angeles, CA 90009

Aerophysics Laboratory

173. A Shock Tube Study of the Reactions of Hydroxyl Radicals with Combustion Species

Cohen, N.

Comm. 213-336-7427

The project objective is to measure the rate coefficients for reactions of OH radicals of special importance for understanding and predicting hydrocarbon combustion. The experiments are being performed in a shock tube at combustion temperatures near 1200 K and near atmospheric pressure. Transition state theory (TST) calculations have been carried out to relate the measurements to other data at lower temperatures so that reliable temperature dependences of the rate coefficients under study can be established. The calculations also assist in the formulation of semiempirical rules for predicting the rate coefficients of species for which data are not available. Experimental measurements of rate coefficients for reactions of OH radicals with hydrogen, methane, ethane, propane, 2,3-dimethylbutane, neopentane, isobutane, isooctane, cyclopentane, ethylene, acetylene, acetone, formaldehyde, methanol, and ethanol have been completed. For most of these, TST calculations have been made. The reaction of OH with methyl radicals has also been studied.

University of Akron
Akron, OH 44325

Department of Chemistry

174. Molecular Eigenstate Spectroscopy: Application to the Intramolecular Dynamics of Some Polyatomic Molecules in the 3000 to 7000 cm^{-1} Region

Perry, D.S.

\$75,580

Comm. 216-375-6825

Two methods of infrared spectroscopy will be developed for the study of the vibrational dynamics of individual polyatomic molecules. To control thermal congestion, the molecules will be supercooled in a nozzle expansion. The first method, frequency-modulated sliced-jet spectroscopy, is ordinary absorption spectroscopy but with a vibrating string in the nozzle expansion which causes a narrow hole in the Doppler lineshape. The second method is a form of double resonance employing two infrared laser beams which will allow the selective recording of spectra of those molecules with a specified set of quantum numbers. In accordance with the uncertainty principle, collisionless intramolecular vibrational relaxation causes infrared spectra to be broadened. The work will resolve sharp lines, called molecular eigenstates, within the broadened absorptions. These molecular eigenstate spectra will yield detailed information about the mechanism and the rate of

relaxation. Comparison with condensed phase relaxation studies on the same systems (ethanol and 2-fluoroethanol) will yield insight into the role of the dense phase in the relaxation process.

Arizona State University
Tempe, AZ 85287

Department of Chemistry

175. Electronic Structure and Reactivities of Transition Metal Clusters

Balasubramanian, K.

\$93,000

Comm. 602-965-3054

The electronic and geometric structural properties of clusters containing heavy atoms serve as models for regions of surfaces. Thus, investigation of the nature and reactivities of small cluster particles provides important clues to the understanding of catalysis and chemisorption. Electronic properties, such as ionization potentials, electron affinities, energy separations of low-lying states, and binding energies of these clusters and their reactivities vary dramatically with size. Many main group and transition metal clusters are under investigation. In particular, theoretical investigations of Au_6 , Ag_6 , Pd_4 , Ir_3 , W_4 , Cu_6 , and Pt_4 are being conducted. The properties investigated are geometries, ionization energies, electron affinities, and the separations of the low-lying electronic states. The electronic properties of metal dimers, such as Ru_2 , Os_2 , Ir_2 , and so forth, are also being studied from which the spectroscopic properties of these metal dimers are obtained. The reactivities of small cluster particles are also investigated with model reactions such as $\text{M} + \text{H}_2$ and $\text{M}_2 + \text{H}_2$. The potential energy surfaces of TaH_2 , ReH_2 , ReH_2^+ , WH_2^+ , OsH_2 , and so forth, are being determined with the objective of understanding the reactivities of these atoms with H_2 . The $\text{Pt}_3 + \text{H}_2$ and $\text{Pt}_3 + \text{H}$ systems are also being studied. These investigations are conducted using a complete active space MCSCF (CASSCF) followed by higher order configuration interaction calculations. Relativistic effective potentials are used for the heavy atoms in the molecule, and spin-orbit and correlation effects are introduced simultaneously through a relativistic configuration interaction (CI) scheme.

University of Arizona
Tucson, AZ 85721

Department of Chemistry

176. Chemical Activation of Molecules by Metals: Experimental Studies of Electron Distributions and Bonding

Lichtenberger, D.L.

\$98,000

Comm. 602-621-4749

This project is directed toward understanding the electronic structure and bonding features of transition metal species that contribute to controlling the reactivity of carbon-containing molecules. The focus of the research is on the development of ionization spectroscopies for the high resolution study of metal-molecule interactions in

the gas phase as well as the study of metal species on surfaces in ultrahigh vacuum. The research also incorporates scanning tunneling microscopy. This technique contributes to the structural characterization of surface morphologies, and in addition is related to the ionization characteristics of the metal species because the tunneling current depends on the orbital electronic structure. In recent months the ionization spectroscopies have been used to investigate metal-alkyl and metal-hydride interactions as a function of the electron-richness at the metal center. These studies are part of a general investigation of carbon-hydrogen bond activation. The electron distribution in metal-acetylide complexes, which is important to the development of conductive polymers and unique optical properties, has also been examined. The surface and gas phase valence photoelectron spectra of buckminsterfullerene, C₆₀, have been obtained, as well as STM images of C₆₀ on gold that reveal the prominent electronic interactions with the metal surface.

**University of California, Los Angeles
Los Angeles, CA 90024**

Department of Chemistry and Biochemistry

**177. High-Resolution Raman Spectroscopy of
Complexes and Clusters in Molecular
Beams**

Felker, P.M.

\$76,221

Comm. 213-206-1274

Mass-selective, ionization-detected stimulated Raman spectroscopy (IDSRS) methods, and Fourier transform versions thereof, have been applied to the study of the vibrational resonances of weakly bound species in molecular beams. These methods rely on resonantly enhanced multiphoton ionization to probe the shifts in state populations induced by stimulated Raman scattering processes. Much of the effort thus far has been directed toward the Raman spectroscopy of benzene dimer and isotopically substituted dimers in the region of the ν_1 totally symmetric C-C stretch fundamental. In addition to benzene dimers higher benzene clusters (i.e., the trimer and tetramer) have also been studied. For all of these species information has been obtained about the lifetimes of the excited vibrational states prepared by ν_1 excitation. High-resolution (0.05 cm⁻¹) Raman spectra have also been obtained for the species. In this regard frequency shifts and splittings caused by the interaction between benzene moieties have been observed. Mixed one-to-one complexes of benzene with atoms or molecules have also been studied. The ν_1 line position shifts of benzene-Ar, benzene-N₂, benzene-CH₄, and others have been measured. Each of these species upon ν_1 excitation lives for nsec or longer, despite the fact that the vibrational excitation is significantly higher in energy than that required to dissociate these weakly bound species. In conjunction with the study of benzene-N₂ and benzene-phenol, the possibility of studying vibrational spectroscopy of solvent species in solute-(solvent)_n complexes with IDSRS methods has been demonstrated, even though probe photoionization proceeds through a solute-localized transition.

**Catholic University of America
Washington, DC 20064**

Department of Chemistry

178. Studies of Combustion Kinetics and Mechanisms

Gutman, D.

\$177,000

Comm. 202-319-5385

The purpose of this research is to gain new quantitative knowledge of the kinetics and mechanisms of the reactions of polyatomic free radicals that are important in hydrocarbon combustion processes. The free radicals are generated in a heated tubular reactor by the decomposition of molecules using pulsed ultraviolet-laser photolysis. The ensuing reactions are monitored in time-resolved experiments using photoionization mass spectrometry. Reaction rate constants are measured as a function of temperature (to 1000 K) and pressure (1 to 20 torr), and the primary reaction products are determined to obtain basic information regarding the fundamental kinetics and dynamics of the reaction under study. This information also provides a rational basis for extrapolating observed kinetic behavior of free-radical reactions to the harsher conditions of actual combustion processes. Reactions under study include recombination of free radicals (e.g., CH₃ + CH₃), unimolecular decomposition of free radicals (e.g., C₂H₅, CH₃CO, and M-C₅H₁₁), and reactions of these same free radicals with molecular oxygen (e.g., C₂H₅ + O₂). In most instances, results obtained are the first quantitative determinations of the kinetic behavior of the reaction under study. When this information is incorporated into global models of combustion chemistry, it provides significant improvements in the reliability of these models to predict major chemical properties of burning processes.

**University of Chicago
Chicago, IL 60637**

James Franck Institute

179. Quantum Dynamics of Fast Chemical Reactions

Light, J.C.

\$88,000

Comm. 312-702-7197

The objectives of this research have been the evaluation of the accurate cross sections and rate constants for fast chemical reactions in the gas phase. Accurate potential energy surfaces are not available for several systems. Research has focused on the direct quantum calculation function approach. Using the Discrete Variable Representation the rate constants are obtained by solving for the eigenvalues and eigenvectors of the Hamiltonian and the thermal flux operators, and evaluating the flux-flux correlation functions for each total angular momentum, J, and evaluating the thermal rate constants for each J at the desired temperatures. The thermal rate constants for the hydrogen isotopic systems have been evaluated and compared reasonably well with experiment using the SLTH potential energy surface, with agreement within a factor of two over a wide temperature range over which the rates vary by several orders of magnitude. Because this direct approach of rate constants is computationally intensive,

improvements via the use of the split interaction representation and optical potentials are under development. The time-dependent self-consistent Hartree approach where only the few reaction coordinates are treated quantum mechanically is also being considered.

University of Colorado Boulder, CO 80309

Department of Chemistry and Biochemistry

180. Laser Photoelectron Spectroscopy of Ions Ellison, G.B. \$102,524 Comm. 303-492-8603

This project uses photoelectron spectroscopy to study the properties of negative ions and radicals. The essence of the experiment is to cross a 0.6 keV mass-selected ion beam (M^-) with the output of a CW laser, $\hbar\omega_0$. The resultant detached photoelectrons with kinetic energy, KE, are energy analyzed by an electrostatic, hemispherical analyzer $M^- + \hbar\omega_0 \rightarrow M + e(KE)^-$. Analysis of the photoelectron spectra permits extraction of molecular electron affinities, vibrational frequencies, and electronic splittings of the final radical, M, as well as the relative molecular geometries of ions (M^-) and radicals (M). During the last year a study of methyleneimine anion, CH_2N^- has been completed. A new hemispherical electrostatic energy analyzer has been constructed. Preliminary spectra taken on this new instrument indicate that a spectral resolution of roughly 10 meV is attainable. The negative ion photoelectron spectra of CH_2N^- and CD_2N^- have been measured, and the following electron affinities have been found: $EA(CH_2N) = 0.511 \pm 0.008$ eV and $EA(CD_2N) = 0.498 \pm 0.011$ eV. The $EA(CH_2N)$ is combined with the results of previous gas phase ion studies to extract a number of thermochemical parameters (kcal/mol): $D_0^0(CH_2N-H) = 85 \pm 5$, $D_0^0(H-HCN) = 23 \pm 6$, and $D_0^0(H_2C=N) = 144 \pm 6$. Attempts to calculate the geometry and vibrational frequencies of the H_2CN radical are disappointing. Unrestricted Hartree-Fock and second order Møller-Plesset *ab initio* calculations in a 6-31++G** basis produce badly spin-contaminated wavefunctions that do not reproduce the experimental findings.

181. Time-Resolved FTIR Emission Studies of Laser Photofragmentation and Chain Reactions Leone, S.R. \$95,000 Comm. 303-492-5128

A time-resolved Fourier transform infrared (FTIR) emission technique is used for the study of molecular photofragmentation processes, energy transfer, and reaction dynamics. The apparatus unites a commercial FTIR spectrometer with a high repetition rate excimer laser. Through the use of time synchronization methods, high performance infrared detectors, and multipass light collection optics, spectra are obtained from a number of molecules and polyatomic radical species following these laser induced processes. The dynamics of the photofragmentation of vinyl chloride, dichloroethylene, chlorofluoroethylene, acetone, acetylene, and ammonia have been studied with vibrational and rotational state detail. Details of the radical spectroscopy are obtained. Single collision energy transfer events and radical-radical

reactions are also studied for the first time with high resolution and time-resolved capability. Results are obtained on the radical-radical reaction of Cl with ethyl radicals. In chain reaction work, the rotational excitation is used as a thermometer for the temperature of the combusting mixture.

Columbia University New York, NY 10027

Department of Chemistry

182. Energy Partitioning in Elementary Gas-Phase Reactions Bersohn, R. \$90,000 Comm. 212-854-2192

Elementary gas-phase reactions, both bimolecular and unimolecular, are being studied by laser generation of reactants and laser-induced fluorescence of the reaction products. Recent experiments have focused on the photodissociation of two molecules, cyclopentadiene and indene. A laser photon of known energy is absorbed by the molecule, and the electronic energy is very quickly converted into vibrational energy. Energy is redistributed within the molecule until ultimately on the time scale of microseconds enough accumulates in a methyl C-H bond to eject a hydrogen atom. A key finding is that the hydrogen atoms have a translational temperature (determined from the Doppler width of the atomic absorption line) that is within experimental error the same as the internal vibrational temperature. The measurement of both H atom kinetic energy and dissociation rate as a function of both internal energy and molecular complexity while the transition state remains fixed has enabled a thorough test of RRKM theory. A strong laser at 121.6 nm is being used to photodissociate molecules and also to detect hydrogen atom fragments. Partially deuterated methanes exhibit H atom/D atom photofragment ratios which are twice the composition ratios, i.e., CH_3D , CH_2D_2 , and CHD_3 have H/D ratios of 6, 2, and 2/3 respectively.

183. Laser-Enhanced Chemical Reaction Studies Flynn, G.W. \$130,000 Comm. 212-854-4162

This project employs extremely high resolution infrared diode lasers to study fundamental combustion and collision dynamics and photochemical reaction processes. High-energy atoms, molecules, and chemically reactive radicals, produced by excimer laser photolysis or dye laser excitation, are used as reagents to investigate collisional excitation, collisional quenching, and chemical production of individual rotational and vibrational states of molecules. Translational energy recoil of the target molecules is probed by measuring the time-dependent Doppler profile of the molecular infrared transitions. Chemical reactions between hot Cl atoms and stable molecules are monitored with quantum state resolution using this diode laser probe method. Reaction between deuterated cyclohexane and Cl atoms produces a DCl product with cold rotational but hot translational degrees of freedom. This suggests a reaction mechanism in which the DCl recoils collinearly along the C-D-Cl axis. Such a mechanism has been observed previously for combustion

reactions involving H atom abstraction from hydrocarbons by O atoms. A similar experimental approach is being used to investigate the chemical dynamics of the reaction between OH radicals and CO molecules to give CO₂ and H atoms. Results obtained so far indicate significant bending vibrational excitation of the CO₂ produced by this reaction suggesting a bent HCO₂ transition state complex. The quenching of highly energetic and reactive O(¹D) atoms by CO₂ through a variety of physical and chemical mechanisms can be studied by the same technique. Some of the electronic energy of the O atom appears to be funneled into rotational and translational degrees of freedom, but very little of the electronic energy goes into CO₂ vibrational excitation. This is quite surprising since the quenching of O(¹D) by CO₂ is quite efficient and has been thought to proceed through a tight CO₃ complex.

Cornell University
Ithaca, NY 14853

Department of Applied and Engineering
Physics

184. Mass Resolved Resonance Ionization Spectroscopy of Combustion Radicals

Cool, T.A. **\$90,000**
Comm. 607-255-4191

Resonance-enhanced multiphoton ionization (REMPI) spectroscopy is well-suited for the ultrasensitive detection of weakly fluorescing flame radicals of key importance in the combustion of hydrocarbons, nitrogen-based propellants, and chlorinated hydrocarbons. Spectroscopic data for Rydberg states of combustion radicals are urgently needed for wider application of REMPI spectroscopy for *in situ*, spatially resolved, flame species density profiles. The primary goal of this research is the discovery and characterization of such electronic states. Progress toward this goal is exemplified by observations of new electronic states in HCO, C₂, and C₂H. A rich ensemble of REMPI bands, assigned to one-photon absorptions in HCO, was observed in the 208 and 258 nm spectral region. These include transitions to the $\tilde{B}(A')$ state, the $3p\ ^2\Pi(A'$ and $A'')$ states, the $3p\ ^2\Sigma^+$ state, and (tentatively) the $3s\ ^2\Sigma^+$ state. All of these bands are much stronger than the previously observed (2 + 1) REMPI spectra of the $3p\ ^2\Pi(A'')$ state; a majority are suitable candidate transitions for REMPI flame diagnostics. A new apparatus, a flame-sampling laser-ionization mass spectrometer, is in use for the mass resolved detection of REMPI ions, formed *in situ*, from laboratory flames. This will permit the correlation of the mass spectra with REMPI electron spectra obtained with an electron collection probe. Assignments of the REMPI electron spectra to the originating flame species will be established, thereby overcoming the primary difficulty presently limiting more widespread use of the REMPI method.

Department of Chemistry

185. State-Resolved Studies of the Methyl Radical

Houston, P.L. **\$121,708**
Comm. 607-255-4303

Reactions of methyl radicals play a major role in the combustion of nearly all hydrocarbon fuels. The project objectives are (1) to examine photodissociations producing methyl radicals in order to learn the internal and translational energy distributions of the products and (2) to develop a capability to investigate important combustion reactions using these methyl radicals as reagents. A detailed examination has been performed for four methyl sources: methyl iodide, acetone, acetaldehyde, and nitromethane. Now that the methyl radicals produced in these dissociations have been characterized, an apparatus is being constructed that will allow examination of specific reactions such as $CH_3 + H_2 = CH_4 + H$, the reverse of this reaction, and $CH_3 + H_2CO = CH_4 + HCO$.

Emory University
Atlanta, GA 30322

Department of Chemistry

186. Theoretical Studies of Combustion Dynamics

Bowman, J.M. **\$86,969**
Comm. 404-727-6592

The objectives of this research project are to provide a detailed understanding of dynamical processes in gas-phase reactivity and energy transfer, and to examine reactions of relevance to combustion. Currently two major projects are under way, reduced dimensionality theory of diatom-diatom reactions and resonances in bimolecular scattering. The reduced dimensionality quantum theory of atom-diatom reaction has been extended to describe diatom-diatom reactions in which one bond is nonreactive. This is quite a general situation for metathesis reactions, such as $OH + H_2 \rightarrow H_2O + H$ and $H_2 + CN \rightarrow HCN + H$. The new theory is based on hyperspherical coordinates for the two degrees of freedom involved in the bond breaking and bond making. The nonreactive degrees of freedom are described using "cylindrical" coordinates that are perpendicular to the plane containing the polar coordinates. Code development is finished, and results on the $H_2 + CN$ have been obtained. Detailed quantum studies of direct and resonant scattering are continuing for the $H + CO$ system, which is serving as a prototype recombination reaction. In addition to the coupled channel scattering calculations that are continuing and focusing on nonzero total angular momentum, L^2 stabilization calculations of resonances have been completed. Also completed are L^2 simulations of the photodetachment spectra of IHI^- and $ClHCl^-$ for zero total angular momentum.

187. Kinetics and Mechanisms of Reactions Involving Small Aromatic Reactive IntermediatesLin, M.-C. **\$92,000**
Comm. 404-727-2825

The kinetics and mechanisms of reactions of C_6H_5 , C_6H_5O , and C_6H_4 are being investigated by resonance absorption (RA) and resonance-enhanced multiphoton ionization (REMPI) techniques using tunable dye lasers. For studies with the RA method, electronic transitions in the visible region will be utilized to monitor these radicals using a reactor with a multiple-reflection cavity. For studies with the REMPI technique, the spectroscopy and kinetics of these radicals will be investigated in the uv/vuv region by means of one-, two- or three-photon enhancement. The kinetics and mechanisms of the reactions important to combustion chemistry will be emphasized in these studies.

Georgia Institute of Technology
Atlanta, GA 30332-0430

School of Physics

188. Reactive Collisions of High-Temperature SystemsGraff, M.M. **\$20,740**
Comm. 404-894-8255

A newly developed experimental technique examines reactivity of neutral systems with large activation barriers using a fast neutral beam. The initial system under investigation is the basic oxygen-hydrogen combustion system $O + H_2 \rightarrow OH + H$. A fast beam of neutrals is produced by photodetachment of the corresponding negative ions within the extended cavity of an argon ion laser. Energetic neutrals then collide with a stable reactant gas in a collision cell. Reaction products are detected by ionization and mass analysis, providing the total (relative) reaction cross section. The beam-cell geometry isolates the contribution of reagent internal excitation from that of translational energy. A temperature-controlled reaction cell minimizes thermal energy, thus allowing a precise study of the structure of the reaction cross section. The effect of rotational excitation will be studied by comparing reactivity for cold para- and normal H_2 . This study significantly augments experimental capabilities for the study of neutral systems with activation barriers.

University of Georgia
Athens, GA 30602

Center for Computational Quantum Chemistry

189. Theoretical Studies of Hydrocarbon Combustion ChemistrySchaefer, H.F., III **\$100,000**
Comm. 404-542-2067

In recent years theoretical chemistry has become a significant source of specific predictions concerning molecular systems that may be very important, but inaccessible to

experiment. An important example is the study of molecular species and chemical reactions of fundamental importance in combustion processes. Reactions being studied using *ab initio* quantum mechanics include $CH_3 + O_2$, $CH_4 + O_2$, $C_2H_5 + O_2$, and $C_2H_6 + O_2$. Other problems of current interest include the reactions of triplet methylene with saturated hydrocarbons, the heats of formation of the C_2H and C_2H_3 radicals, the infrared spectra of CH_5^+ and $C_2H_5^+$, quantitative theoretical predictions of infrared and Raman spectral intensities, the characterization of keto-carbenes, the understanding of the relationship between the two nearly degenerate isomers of the HO_2 dimer, hydrocarbon rearrangements on small metal clusters (especially aluminum), and the nature of hydrated hydronium clusters.

Department of Chemistry

190. Photodissociation and Spectroscopy of Gas Phase Bimetallic ClustersDuncan, M. **\$68,987**
Comm. 404-542-1998

Metal cluster molecules composed of a variety of two component mixtures are produced in a molecular beam using laser vaporization-pulsed nozzle techniques. In general, these bimetallic clusters exhibit many of the same fascinating properties observed for pure component metal clusters. However, bimetallics provide the additional opportunity to study condensation dynamics and bonding patterns not possible with single component systems. This project focuses on the photodissociation dynamics and spectroscopy of bimetallic mixtures of silver, aluminum, or bismuth with the transition metals chromium and iron. These systems are studied with mass selected ion photodissociation spectroscopy and resonant laser photoionization spectroscopy in a supersonic molecular beam time-of-flight mass spectrometer system. These measurements provide cluster rotational, vibrational, and electronic energy levels and dissociation energies as a function of cluster size. This project represents a unique approach to the study of novel cluster systems with significant implications for metal bonding theory and theoretical models of catalysis.

Harvard University
Cambridge, MA 02138

Division of Applied Sciences

191. Fundamental Studies of Carbenes and Hydrocarbon RadicalsThaddeus, P.; Gottlieb, C. **\$105,500**
Comm. 617-495-7340

This project comprises fundamental millimeter-wave spectroscopy of highly reactive carbenes, carbon-chain radicals, and ring-chain hybrids produced in low-pressure discharges through flowing mixtures of combustion gases. The purpose is to provide definitive spectroscopic identification, accurate spectroscopic constants in the lowest vibrational states, and accurate structures of the key intermediates in reactions leading to aromatic hydrocarbons and soot particles in combustion. This year rotational spectra of the cumulene carbenes propadienyldiene

(H₂CCC) and butatrienylidene (H₂CCCC) were observed for the first time, and their structures are now being determined from isotopic substitution; the shallow decrement in intensity between these two carbenes suggests that higher members in the series also are detectable. Nearly all the lower vibrationally excited states of C₄H and C₄D have been measured, yielding spectroscopic constants that should greatly aid assignment of the infrared spectrum of gaseous C₄H, when observed. The rotational spectrum of the propenonyl radical (HCCCO), a floppy molecule with a strongly perturbed ground state (recently encountered in kinetic studies of CCH with CO), has been detected and its hyperfine structure observed in ¹³C-substituted HCCCO.

Department of Chemistry

192. Laser Spectroscopy of Hydrocarbon Radicals

Chen, P.

\$86,278

Comm. 617-495-1842

Supersonic jet-flash pyrolysis of peroxyesters is used to generate cold organic free radicals in the gas phase for spectroscopic characterization. Vacuum ultraviolet (VUV) laser time-of-flight and photoelectron spectrometry have been used to determine the heat of formation of cyclopropenylidene, c-C₃H₂, via its adiabatic ionization potential. The value of $\Delta H_{f}[c-C_3H_2] = 114 \pm 4$ kcal/mol is used to show the validity of a valence-bond model for radical bond strengths. The homolytic bond dissociation energies for cyclopropenyl, c-C₃H₃, is predicted to be 60 kcal/mol, and found to be 61 ± 6 kcal/mol from the data above. Photoelectron spectra are also obtained for vinyl radical, C₂H₃, and a totally deuterated isotopomer. The Franck-Condon envelope of the photoelectron spectra is interpreted by comparison to *ab initio* predictions of the surface for vinyl cation. Photoelectron spectroscopy for propargyl radical, 1-C₃H₃, and two partially deuterated isotopomers, confirm the electron impact value for the ionization potential to within experimental error. A single active vibration in the spectrum is found to be extremely anharmonic, with Morse parameters, $\omega_e = 2270$ cm⁻¹ and $\omega_e x_e = 130$ cm⁻¹. The vibration is assigned to the acetylenic C...C stretch in propargyl cation whose anharmonicity derives from configuration interaction of the dominant "acetylenic" propargyl wavefunction with an "allenic" structure at higher energies.

University of Illinois at Chicago Chicago, IL 60680

Department of Chemical Engineering

193. Kinetics of Combustion-Related Processes at High Temperatures

Kiefer, J.H.

\$94,000

Comm. 708-996-9430

The purpose of this project is to determine rates and mechanisms for fuel hydrocarbon pyrolysis at high temperatures. The measurements are made in a shock tube (providing arbitrary, precise, and externally set temperatures) with two very high resolution laser diagnostic techniques: laser schlieren measurement of density gradients (net endothermic rate) and the new method of

excimer laser flash absorption, which provides absorption profiles in the ultraviolet with 0.05 microsecond resolution. Previous work has defined much of the pyrolysis kinetics of ethylbenzene, pyridine, cyclohexene, toluene, benzene, and 1,3-butadiene. Flash absorption measurements at 220 nm have confirmed the laser schlieren rate for 1,3-butadiene dissociation. A study of the dissociation of vinylacetylene has led to the proposal of a new mechanism for acetylene polymerization, and this mechanism has now been employed in a successful modeling of both previous and new shock tube data on this reaction. Current work centers on the study of allene/propyne pyrolysis, the decomposition of formaldehyde, some new measurements of acetylene pyrolysis, and further investigation of falloff effects in large-molecule dissociation.

Department of Chemistry

194. Kinetics of Elementary Atom and Molecule Reactions

Gordon, R.J.

\$95,000

Comm. 708-996-3280

The project objective is to study the chemical reactions and energy transfer rates of atoms and small molecules. Recent efforts have dealt with laser diagnostic measurements of oxygen atoms, the production and relaxation of multiplet states of oxygen atoms, and the quenching of electronically excited carbon monoxide. Laser-induced fluorescence measurements of triplet oxygen atoms using 845 nm detection can lead to systematic errors in the fine structure population and to nonlinearity in the apparent concentration. The behavior is attributed to amplified spontaneous emission (ASE) between the 3P and 3S levels; a kinetic model to explain it has been developed. In a second study, the multiplet state distribution of triplet oxygen atoms produced by the photodissociation of oxygen, carbon dioxide, and sulfur dioxide was measured. Nonstatistical distributions were observed for oxygen and carbon dioxide, while a statistical distribution was observed for sulfur dioxide. Mechanisms based on the electronic structures of these molecules have been proposed. In a third study the fluorescence of CO excited to the Rydberg B state at 115 nm was monitored in real time, and the rate of quenching of this state by H₂, D₂, He, Ne, Ar, Kr, Xe, N₂, O₂, HF, and HCl as collision partners was measured. An unusual increase in the non-resonant fluorescence upon addition of argon gas has been observed and is being explored.

Johns Hopkins University Baltimore, MD 21218

Department of Chemistry

195. Theoretical Studies of Nonadiabatic and Spin-Forbidden Processes: Reactions and Spectroscopy of Radical Species

Yarkony, D.R.

\$117,500

Comm. 301-338-4663

This research program will focus on studies of spin-forbidden and electronically nonadiabatic processes involving radical species that are relevant to combustion

reactions and combustion diagnostics. To study the electronic structure aspects of these processes a unique and powerful system of electronic structure programs developed over the past six years, the BROOKLYN, codes will be employed. These programs enable addressing questions basic to the understanding of elementary combustion chemistry processes which are not tractable using more standard quantum chemistry codes. Particularly relevant to the proposed research are the capabilities (1) to treat the spin-orbit interaction within the context of the full microscopic Breit-Pauli approximation and (2) to use analytic gradient techniques to determine the interstate derivative couplings that result in the breakdown of the single surface Born-Oppenheimer approximation and to locate seams of actual/avoided crossings and minimum energy crossings of potential energy surfaces. In conjunction with the electronic structure calculations, dynamics studies will also be performed, using classical trajectory based, as well as fully quantum, techniques. This combination of nonadiabatic, electronic structure and dynamics, techniques will provide the opportunity for important contributions to the understanding of nonadiabatic combustion processes. The goals of this research program are then, to study several problems concerning the chemistry of free radical species which are of importance in combustion reactions and combustion diagnostics, and to enhance the computational capabilities of the BROOKLYN system of programs. This research effort will consider: (1) collisional quenching of the electronically excited radical species $\text{NO}(A^2\Sigma^+)$ and $\text{OH}(A^2\Sigma^+)$; (2) fine structure changing collisions: $\text{OH}(^2\Pi_{3/2,1/2}) + \text{Ar}$, $\text{CH}(^2\Pi_{3/2,1/2}) + \text{He}$ and $\text{CH}(^2\Pi_{3/2,1/2}) + \text{Ar}$; (3) spin-orbit coupling effects in the reaction $\text{OH}(^2\Pi\Omega) + \text{O}(^3P_J) \rightarrow \text{HO}_2(^2A'')^* \rightarrow \text{H}(^2S) + \text{O}_2(X^3\Sigma_g^-)$; and (4) nonadiabatic effects in excited Rydberg states accessed in resonance enhanced multiphoton ionization (REMPI) detection schemes of flame species including the C_2 and HCO systems as well as other radicals present in combustion environments including C_2H and CH_2 .

**University of Kentucky
Lexington, KY 40506-0055**

Department of Chemistry

196. Laser Spectroscopy and Dynamics of Transient Species Formed by Pyrolysis Reactions
Clouthier, D.J. **\$66,000**
Comm. 606-257-1790

The spectroscopy and excited-state dynamics of transient species formed by pyrolysis reactions are currently under investigation. The major experimental technique is pyrolysis jet spectroscopy, in which precursor molecules are pyrolyzed in the throat of a supersonic nozzle and then rapidly expelled into a vacuum. Laser-induced fluorescence is used to detect and characterize the jet-cooled pyrolysis products. A major study of the S_1-S_0 and T_1-S_0 spectra of thioformaldehyde has been completed and excited state bending potentials determined. The S_1 state decay dynamics have also been extensively studied under collision-free conditions. Spectra of the HCCS and DCCS free radicals have been acquired and are being analyzed. Rotationally resolved spectra of dichlorocarbene have

yielded the ground and excited state geometries, symmetries, and multiplicities. Studies of the N_2S , C_2S , HCCO , and C_3O transient species are in progress.

**Massachusetts Institute of Technology
Cambridge, MA 02139**

Department of Chemical Engineering

197. Aromatics Oxidation and Soot Formation in Flames
Howard, J.B. **\$108,100**
Comm. 617-253-4574

The oxidation of aromatics and the formation of soot in flames are being studied with emphasis on mechanisms and kinetics of the dominant reactions. The research includes experimental measurement of profiles of stable and radical gas species concentrations through the reaction zone of low-pressure one-dimensional flames. The oxidation of benzene and other aromatic compounds by hydroxyl radicals and oxygen atoms is studied by introducing the aromatic compound as a fuel additive in hydrogen-oxygen flames whose OH and O concentrations profiles are experimentally well-known. A molecular-beam-sampling instrument, with on-line mass spectrometry and water-cooled probe sampling with cryogenic trapping followed by GC, GC/MS, FTIR, and NMR analyses, is being used to study gases including high molecular weight compounds. Soot particles are being studied by solvent extraction techniques. Net reaction rates calculated from the data are used to test hypothesized reaction mechanisms. Probe samples from the soot-particle inception zone of a flame have been found to include high molecular weight compounds of up to 1000 amu and larger, containing alkyne, alkene, and alkane structures. Substantial quantities of fullerene compounds such as C_{60} and C_{70} are produced with the soot under certain flame conditions.

Department of Chemistry

198. Spectroscopic and Dynamical Studies of Highly Energized Small Polyatomic Molecules
Field, R.W.; Silbey, R. **\$140,000**
Comm. 617-253-1489

Stimulated Emission Pumping (SEP) and Optical-Optical Double Resonance (OODR) spectra of acetylene (HCCH) and formyl radical (HCO) have been recorded. The acetylene SEP spectra contain information about the evolution from regular to chaotic dynamics, the location of acetylene-vinylidene isomerization resonances on the lowest singlet potential surface, and the structure of the lowest triplet state of the *cis*-bent acetylene surface. The acetylene OODR spectra have characterized two new, pre-dissociated singlet states (one planar *trans*-bent with a nominal C-C single bond, one nonplanar near *trans* with a nominal C-C double bond). The HCO SEP spectra sample mode specific lifetimes of several vibrational resonances on the ground state surface that lie more than 4000 cm^{-1} above the $\text{HCO} \rightarrow \text{H} + \text{CO}$ dissociation limit; these resonances are relevant to the efficiency of collisional stabilization of HCO. Stark and Zeeman quantum beat and anticrossing spectra of acetylene have located the planar

cis→*trans* isomerization barrier on one of the two lowest triplet potential surfaces.

**University of Massachusetts at
Amherst
Amherst, MA 01003**

Department of Chemical Engineering

- 199. Probing Flame Chemistry with MBMS,
Theory, and Modeling**
Westmoreland, P.R. **\$83,000**
Comm. 413-545-1750

Detailed flat-flame data allow testing predictions of kinetics for individual reactions from comprehensive mechanisms. Radical and stable-species data from molecular-beam mass spectrometry (MBMS) can be analyzed to yield net reaction rates for each species throughout the flame. The wide range of temperatures and reactant concentrations permits tests of theoretical rate constants and whole-flame mechanistic modeling. Kinetics and branching of individual reactions are predicted and extrapolated with Quantum-RRK and RRKM methods, and flame structures are predicted using modifications of the Sandia PREMIX/Chemkin codes. Work for this project will focus initially on oxidation and molecular-weight growth in low-pressure propene flames.

Department of Chemistry

- 200. Theory of the Dissociation Dynamics of
Small Molecules on Metal Surfaces: Finite
Temperature Studies**
Jackson, B.E. **\$68,278**
Comm. 413-545-2583

Studies of the dissociative adsorption of diatomics on metals can tell us much about metal catalyzed reactions. Proper theoretical treatments have been hindered by the difficulty of including all important degrees of freedom quantum mechanically. In earlier studies, efficient time dependent methods were developed for surmounting these problems. During this past year models were implemented in which molecular vibration, rotation, and translation normal to the surface were treated quantum mechanically. Probabilities for dissociative sticking and rotational excitation were computed as a function of the kinetic and internal energy of the molecule, as well as the surface impact site. Comparisons were made with earlier studies of lower dimensionality. The remaining degrees of freedom are now being included classically in a comparison with experimental studies of H₂, N₂, and O₂. Techniques that were developed for coupling the gas particle to the thermal vibrations of the solid were used to study trapping. Sticking probabilities were computed for He, Ne, and Ar over a wide range of temperatures, kinetic energies, impact angles, and gas-surface potentials. These techniques are now being used to examine the trapping of H₂ and other diatomics in the weak precursors often found in dissociative adsorption pathways.

**University of Michigan
Ann Arbor, MI 48109-2143**

**Department of Atmospheric, Oceanic, and
Space Sciences**

- 201. Energy-Transfer Properties and Mechanisms**
Barker, J.R. **\$149,346**
Comm. 313-763-6239

This project studies the mechanisms and properties of collisional energy transfer involving moderate-sized molecules. The project objectives are to gain a fuller understanding of highly vibrationally excited molecules by a combination of experiments and theoretical investigations, and to develop a workable theoretical model of the energy-transfer process. In the experimental investigations, various techniques are used to monitor energy in the excited molecules, or energy transferred to a collision partner. The techniques include time- and wavelength-resolved infrared fluorescence, optoacoustics, time-dependent thermal lensing, and multiphoton ionization. In order to determine the mechanisms of energy transfer, homologous series of molecules and isotopomers are investigated to examine the effects of dipole moments, symmetry properties, fundamental vibrational frequencies, internal rotors, and so forth. In the theoretical effort, improved methods are being developed for calculating internal state sums and densities for nonseparable degrees of freedom. Collisional/reaction master equation calculations are carried out to investigate the manifestations of energy transfer under extreme conditions, such as in shock-heated gases.

**University of Minnesota
Minneapolis, MN 55455**

Departments of Chemistry and Physics

- 202. State-to-State Dynamics of Molecular Energy Transfer**
Gentry, W.R.; Giese, C.F. **\$115,000**
Comm. 612-625-2894

The transfer of energy between molecules is an intimate part of virtually every dynamical process in chemistry. It is a particularly important aspect of combustion dynamics in the gas phase, because the energy released in combustion reactions is large, and because the redistribution of that energy among the reacting molecules can profoundly influence their rates of reaction in subsequent steps. In this project, molecular energy transfer phenomena are being studied at the most fundamental level possible, by the observation of discrete changes of quantum states in single bimolecular collisions at precisely controlled kinetic energies. Focus is on the vibrational and rotational energy transfer in collisions of polyatomic molecules with atoms. So far three different polyatomics have been examined, each of which exhibits different dynamical phenomena. Excitation of ground-state molecules can be highly mode-selective, with coupling between vibrational and rotational degrees of freedom which is indicative of the specific collision geometries which lead to excitation of a

selected mode. Recent work extends these studies by incorporating into the experiments the additional capability of studying transfer of energy from selectively prepared excited states of molecules. The latter experiments employ lasers both to prepare the initial state and to probe the final state after the collision. Concurrently, theoretical investigations of the vibrational and rotational dynamics in each system are also being pursued.

Department of Chemistry

203. Variational Transition State Theory

Truhlar, D. \$94,000
Comm. 612-624-7555

This project is concerned with the development and applications of generalized transition state theory and multidimensional semiclassical tunneling approximations to chemical reaction rates. Several practical versions of variational transition state theory (VTST) have been developed and implemented, as have several accurate tunneling approximations. The methods have been applied to thermal rate constants, using transmission coefficients based on ground-state tunneling, and adiabatic and diabatic extensions have also been presented and applied to calculate rate constants for vibrationally excited reactants. Reliable methods have been developed for calculating chemical reaction rate constants that remain practical even for reasonably complicated molecules; they are being applied to reactions of polyatomic molecules and clusters. New methods for the analysis of secondary deuterium kinetic isotope effects are also being developed. Another important aspect of this work is the development of algorithms for calculating reaction rates on the basis of limited electronic structure information. Both interpolation procedures and direct dynamics methods are under development. New methods for including anharmonicity and for modeling force fields are being developed as well. A general, portable computer program, POLYRATE, has been developed and has been submitted to Quantum Chemistry Program Exchange.

National Institute of Standards and Technology, Gaithersburg Gaithersburg, MD 20899

Chemical Science and Technology Laboratory

204. Kinetics Database for Combustion Modeling

Herron, J.T. \$99,000
Comm. 301-975-2569

The goals of this project are to compile data on all aspects of gas-phase thermal reactions relevant to basic energy sciences, to evaluate subsets of the compiled database to provide a chemical kinetic database for combustion chemistry, and to make these data compilations and evaluations available to the user community through archival publications, reports, and databases for use on personal computers. Data evaluation is the core of the program. The strategy has been to start with methane and then add increasingly more complex fuel type molecules to the database, which now includes data for hydrocarbon molecules

through C₄, oxygen containing species, unsaturated compounds, and related free radicals. Over 1200 elementary reactions are now included in the database. Current activities involve the further expansion of the work on unsaturated compounds with the evaluation of data on the reactions of allene and propargyl. Future plans are to continue to extend the database to include alkynes, aromatic, and heterocyclic species. Eventually the database will also need to provide data for nitrogen- and sulfur-containing species related to pollutant formation.

Physics Laboratory

205. Laser Studies of Chemical Dynamics at the Gas-Solid Interface

Cavanagh, R.R.; King, D.S. \$83,000
Comm. 301-975-2368

The focus of the present research is on laser diagnostics of molecular desorption from surfaces. Both optically and thermally driven processes are examined, using quantum state specific detection to characterize the details of the energy transfer process. Recent experiments have probed laser-induced desorption of NO from Pt(111) and Si(111). A range of desorption laser wavelengths (from 1907 to 355 nm) can be used to stimulate desorption processes, providing insight into the nature of the excited states involved in the desorption process. Population distributions of the desorbed NO molecules (translational, vibrational, rotational, and spin-orbit) are then probed to clarify the details of the energy transfer process. On metal substrates, hot electron mediated desorption has been demonstrated. On Si(111), a coverage dependence in the desorption process has been observed that involves surface states of the (7 x 7) reconstructed surface at low coverage and bulk carriers at high coverage. These state-resolved measurements are providing the basis for understanding optically excited, carrier-driven processes at surfaces, leading to new insights into fruitful strategies for laser-driven surface reactions. Current work is directed at establishing the importance of excited carriers for other simple adsorbates (such as CO) and for more complex molecular adsorbates (such as Mo(CO)₆).

206. Spectroscopic Investigation of the Vibrational Quasi-Continuum Arising from Internal Rotation of a Methyl Group

Hougen, J.T. \$83,000
Comm. 301-975-2379

This project focuses on phenomena related to the vibrational quasi-continuum. Acetaldehyde was chosen for the study because methyl groups are known to be important promoters of intramolecular vibrational relaxation, and because the carbonyl group offers the possibility of both vibrational and electronic probing. The investigation has three parts: (1) understanding the "isolated" internal-rotation motion below, at, and above the barrier; (2) understanding traditional vibrational fundamental and overtone states; and (3) understanding interactions involving levels with multiquantum excitation of both kinds of motion. The microwave transitions in the ground state CH₃CHO, demonstrating that previous v=O problems arose from incorrect data rather than incorrect theory, have been measured. Similarly, remeasurements in the first excited torsional state have been made but new theory is needed and such work has begun. The large

pressure broadening in three low-lying vibrational modes may have a contribution from collision assisted energy transfer. A search for any large pressure-broadening dependence on torsion-rotation quantum numbers will be made in order to shed light on any methyl group role in collisionally induced energy transfer.

**University of New Orleans
New Orleans, LA 70148**

Department of Chemistry

207. Identification and Temporal Behavior of Radical Intermediates Formed During the Combustion and Pyrolysis of Gaseous Fuels

Kern, R.D., Jr. **\$77,000**
Comm. 504-286-6847

The thermal decompositions of acetylene and diacetylene occupy important roles in the soot formation process at high temperatures. Although these reactions have been studied extensively, the complete chemical mechanism has not been established satisfactorily. Recent theoretical and spectroscopic determinations of the carbon-hydrogen bond energy in acetylene have forced a serious reexamination of the rate constants and thermochemical data used for modeling the various concentration profiles for the major and minor products for dilute mixtures of acetylene and of diacetylene in an excess of hydrogen. Time-of-flight mass spectrometry was employed to analyze dynamically the fuel-inert gas mixtures in the reflected shock zone over a wide temperature range. The resulting concentration profiles were fit successfully with a new 85 step mechanism which incorporated the most recent consensual value for the acetylene bond energy, 131 kcal/mol. It was necessary to recalculate the entropy values for the ethynyl radical and to assess the effects of the magnitude of electronic energy level separation. A similar analysis of the thermochemistry appears necessary for the C_4H radical in order to achieve a more complete understanding of the detailed mechanism for the thermolyses of acetylene and the polyacetylenes.

**University of North Carolina at
Chapel Hill
Chapel Hill, NC 27599-3290**

Department of Chemistry

208. PEPICO Studies of Ion Dissociations: The Structure and Heats of Formation of Ions, Molecules, and Free Radicals

Baer, T. **\$100,000**
Comm. 919-962-1580

This research is concerned with the structure and energetics of molecules, ions, and free radicals. The experimental technique applied to the elucidation of structures and energetics is that of photoelectron-photoion coincidence (PEPICO). The primary information obtained from these experiments are ionization energies, fragment ion appearance energies, ion dissociation rates as a function

of the ion internal energy, and the product kinetic energy release distributions. Although the measured particle is always an ionic species, much of the information associated with the reaction $AB \rightarrow A^+ + B + e^-$, is related to neutral species through the thermochemical cycle involving the heats of formation of the three species, including the free radical (B). The results of this research will lead to new values for the heats of formation for species important in combustion reactions such as free radicals. In addition to thermochemical information, the research also advances the basic understanding of chemical kinetics. Thus, tunneling through H atom transfer barriers is investigated both experimentally and theoretically through *ab initio* molecular orbital calculations of reaction paths. In addition, the analysis of clusters by ionization methods is critically evaluated by the PEPICO method. In particular, a method to determine whether a given cluster ion is produced directly from the ionization of that neutral cluster, or whether it is produced by a dissociative ionization of a higher order cluster has been developed.

**University of Pennsylvania
Philadelphia, PA 19104**

Department of Chemistry

209. Unimolecular and Bimolecular Reactions Induced by State-Specific Vibrational Excitations

Dai, H.-L. **\$105,000**
Comm. 215-898-5077

A transient vibrational spectroscopic method, Flash Photolysis Stimulated Emission Pumping, was developed for the study of CH_2 and CD_2 . Methylene, an important species in combustion processes, was generated from ketene photolysis. Rotational levels of high bending vibrational overtones \bar{a}^1A_1 CH_2 were characterized in detail. Spectroscopic analyses gave the vibrational term values and rotational constants. The latter were found to be strongly J and K_a dependent suggesting the inadequacy of the rigid rotor Hamiltonian for calculating the rotational energy to high accuracy. Effects of Coriolis, Fermi, and singlet-triplet perturbations were all observed in the spectra along with abnormally intense $\Delta K_a = 3$ transitions. From fitting the experimentally measured bending vibrational term values by a WKB model calculation, the barrier height to linearity in the \bar{a} state was determined to be 9870 cm^{-1} . For CD_2 , rotational constants and vibrational term values of both the \bar{a}^1A_1 and \bar{b}^1B_1 electronic states have been determined. Perturbations to the \bar{a} state rotation-vibration level energies caused by singlet-triplet coupling appeared to be more prominent in CD_2 than in CH_2 . The ratio of the $\Delta K_a = 3/\Delta K_a = 1$ transition intensities is compared with the ones of the CH_2 transitions. This allows assessment of the importance of the Renner-Teller effect in inducing the abnormally strong $\Delta K_a = 3$ transitions. Presently, a time-resolved Fourier transform emission spectroscopic method is being developed to further the existing capability of detecting and characterizing transient species. Combining the laser-induced fluorescence technique with a Fourier transform spectrometer operating in the step-scan mode, this method will eventually allow the detection of fluorescence spectra, from uv to ir, from a transient species with a lifetime of 10^{-8} sec.

Present capability of studying combustion processes that involve many transient species will be greatly enhanced.

Princeton University
Princeton, NJ 08544-1009

Department of Chemistry

210. Spectroscopy and Reaction Dynamics of Collision Complexes Containing Hydroxyl Radicals

Lester, M.I. **\$93,000**
Comm. 215-898-4640

The goal of this program is to obtain a detailed picture of the intermolecular potential between the open-shell hydroxyl radical and various collision partners. To date, laser-induced fluorescence, infrared overtone spectroscopy, and stimulated emission spectroscopy have been used to examine the attractive well regions of the interaction potential between Ar and OH in the ground $X^2\Pi$ and excited $A^2\Sigma^+$ electronic states. Vibrational excitation of the OH moiety may induce dissociation of the complex, providing a means to probe the dynamics taking place on these potential energy surfaces. The results have shown surprising differences, in both the potentials and the dynamics, between the ground and excited electronic states. Most recently, stimulated emission spectroscopy has been used to measure the frequencies of the intermolecular bending and stretching modes in the ground electronic state of the OH-Ar complex correlating with OH ($X^2\Pi$) + Ar (1S_0). A comparison with the bound states calculated from an *ab initio* potential energy surface shows encouraging agreement between theory and experiment, particularly for the bending vibrations.

212. Analysis of Forward and Inverse Problems in Chemical Dynamics and Spectroscopy

Rabitz, H.A. **\$131,987**
Comm. 609-258-3917

This research is concerned with a quantitative exploration of the relationship between structure in intermolecular potential surfaces and resultant observable laboratory behavior. The research has two components. In analysis of dynamics and spectroscopy, a well-defined set of hierarchical (forward) steps are known to lead from the most basic electronic interaction level up to observable spectroscopic and dynamical processes. In recent years, new computational methods have made possible practical calculations along this hierarchy and this aspect of the research is concerned with analyzing the interrelationships between information along the flow through the use of advanced sensitivity analysis techniques. The ultimate aim is an understanding of how macroscopic observables are influenced by detailed structure in the underlying fundamental molecular potentials as well as orbital structure at the electronic level. The research described above aims to provide a means for maximally extracting the physical information content from theoretical studies, but it also indirectly provides a basis to establish practical and numerically stable algorithms for inverting laboratory data back to more fundamental information. In particular, the forward sensitivities generated for analysis may be used to form the kernel of an iterative inversion process. The techniques are specifically designed to be stable and capable of yielding potential information free of imposed model forms.

University of Pittsburgh
Pittsburgh, PA 15260

Department of Chemistry

211. Quantum State Resolved Desorption of CO from Solid Surfaces

Janda, K.C.
Comm. 412-624-8680

A study of the reactivity of carbon monoxide on a potassium promoted Ni single crystal surface has been completed. Although the bond energy of carbon monoxide is very large in the gas phase, and thus the molecule is quite unreactive as a gas, a potassium promoted surface serves as a catalyst for breaking the bond and increasing the reactivity of the molecule. The first measurement of the rate of isotopic mixing between carbon monoxide molecules on such a surface was made. The results were quite surprising in that the activation energy for this reaction is only 67 kJ/mol, yet the reaction does not go to completion in a statistical sense. The results were interpreted in terms of an etherate intermediate with the stoichiometry $K_2C_2O_2$. Current work is aimed at directly observing this proposed species.

Department of Mechanical and Aerospace Engineering

213. Comprehensive Mechanisms for Combustion Chemistry: An Experimental and Numerical Study with Emphasis on Applied Sensitivity Analysis

Dryer, F.L. **\$85,000**
Comm. 609-258-5206

An atmospheric pressure flow reactor (APFR) and a new variable pressure flow reactor (VPFR) facility are utilized to study homogeneous combustion chemistry over a wide range of conditions: pressure, 1 to 15 atm; temperature, 650 to 1200 K; and reaction time, 10 to 20,000 ms. Gas sampling of stable reactant, intermediate, and product species concentrations provides substantial definition of the phenomenology of reaction mechanisms as well as a very constrained set of pure kinetic information to be compared with numerical models. Analytical techniques used for detecting hydrocarbons and carbon oxides presently include gas chromatography, gas chromatography/mass spectrometry, nondispersive infrared, and Fourier transform infrared spectrometry. The VPFR is presently being adapted for resonance absorption measurements of OH. The modeling aspects of the program emphasize the use of hierarchical mechanistic construction along with path and

elemental gradient sensitivity analyses in developing detailed kinetic mechanisms and determining elementary rate parameters through perturbation studies of the CO/H₂/oxidant systems by small amounts of additives. Chemical issues of particular interest include perturbations of the CO/H₂/O₂ system to study the chemistry of HO₂ reactions, the pyrolysis and oxidation mechanisms of simple aldehydes, the pyrolysis and oxidation mechanisms of simple alcohols, and the pyrolysis and oxidation mechanisms of simple olefins.

214. Aromatic-Radical Oxidation Kinetics

Glassman, I.; Brezinsky, K. **\$85,630**
Comm. 609-258-5199

Cyclopentadiene represents a class of species that appears frequently in the combustion of aromatics: long-lived resonantly stabilized compounds. Not only are the oxidation and thermal decomposition of such species interesting in their own right, but their presence in the reaction mixture greatly alters the rates and routes of the combustion process. The current high-temperature flow reactor study of the oxidation and pyrolysis of cyclopentadiene (Cpd) permits examination of the initial reaction steps of the stable parent and some of the postulated steps for the reaction of the cyclopentadienyl radical—an effort crucial to achieving one of the program's ongoing research goals: accurate modeling of aromatic oxidation processes. The initial results of the oxidation study of cyclopentadiene have indicated that there are unique, important major differences between the oxidation of Cpd and previously studied hydrocarbons. Carbon dioxide is produced early in the reaction sequence even before CO has reached its maximum concentration, the point at which rapid CO₂ production usually begins. Consequently, the temperature profiles indicate that the formation of CO₂ is not accompanied by any measurable temperature rise although its production is usually a major source of energy release. Even more unusual is that the concentration of CO₂, for a given time or extent of reaction, increases with increasing equivalence ratio. The fundamental chemistry responsible for these unexpected results is being investigated.

**Rensselaer Polytechnic Institute
Troy, NY 12180-3590**

Department of Chemical Engineering

215. Kinetic Measurements on Elementary Fossil Fuel Combustion Reactions over Wide Temperature Ranges

Fontijn, A. **\$75,000**
Comm. 518-276-6508

The goal of this project is to provide accurate data on the temperature dependence of the kinetics of elementary combustion reactions in order to gain a better fundamental understanding and predictive ability of the chemistry involved, and to serve combustion modelers. Experimental measurements are made by the high-temperature photochemistry (HTP) technique, which allows observations on single reactions in isolation in the 300 to 1800 K range. Studies of a series of reactions of oxygen atoms with H₂, D₂, the C₂-hydrocarbon molecules, propylene, butene-1, benzene, and hydrogen chloride have been completed.

Quantum-mechanical tunneling is found to be an important contributing factor to the rate coefficients of several of these reactions. The experiments have been mainly made by using flash lamp photolysis through one of a number of short wavelength cut-off filters. For several further reactions it has been found that the monochromaticity and/or the shorter pulse duration of laser photolysis is required. The reaction of benzene with O atoms is the first HTP study made in that manner, by using ArF excimer radiation to produce O atoms from SO₂. The plan is to extend this method to other reactions, which were previously found to require techniques other than flash photolysis.

**Rice University
Houston, TX 77251**

Department of Chemistry

216. Infrared Absorption Spectroscopy and Chemical Kinetics of Free Radicals

Curl, R.F., Jr.; Glass, G.P. **\$83,000**
Comm. 713-527-4816

This research is directed at the detection, monitoring, and study (by infrared absorption spectroscopy) of the chemical kinetic behavior of small free-radical species thought to be important intermediates in combustion. In the Miller mechanism for the thermal deNO_x process, HNO production is predicted by the reaction sequence NH₂ + NO → HN₂ + OH, HN₂ + NO → HNO + N₂. A search was made for the HNO molecule in the reaction system NH₂ + NO at room temperature using diode laser infrared kinetic spectroscopy to search for NH stretch absorptions of HNO. No HNO attributable to the deNO_x process was observed. Sensitivity calibration measurements set an upper bound of 1% for the conversion of NH₂ into HNO. The high-resolution infrared spectrum of the heavy atom anti-symmetric stretch of the ketyenyl radical (HCCO) has been observed by means of infrared kinetic spectroscopy. Individual rovibrational transitions have been identified near the band origin located at approximately 2023 cm⁻¹. A second order rate constant of 3.9(5) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ was obtained for the reaction of ketyenyl with NO.

217. Supersonic Bare Metal Cluster Beams

Smalley, R.E. **\$100,000**
Comm. 713-527-4845

Two major advances were made over the past year in this research on bare metal clusters. The first was the discovery of a new type of spectral approach to these metal clusters: vibrational autodetachment from image-charge-bound (ICB) states of the outermost electron of negative metal clusters in the gas phase. The first such example was discovered to be the sixth cluster of gold, Au₆⁻, where high resolution spectroscopy of these ICB states reveals that the gold atoms have the geometry of a flat, perfectly symmetrical hexagonal ring. The outermost electron appears to orbit around the outside of the molecule, attracted by the induced polarization (image charge) in the gold ring. Vibrational autodetachment from these states gives rise to a nicely high resolution spectroscopy which may be quite generally applicable to metal clusters. The second advance was the detailed study of laser-induced transformations between geometrical isomers of transition metal clusters. Certain metal cluster ions such as

Ta₁₀⁺ and Nb₁₉⁺ were shown to be produced in a mixture of two forms, one which was completely inert toward H₂ dissociative chemisorption, the other being reactive on nearly every collision. Using laser annealing techniques on the levitated clusters it was possible to demonstrate interconversion. This now provides one of the most vivid demonstrations yet of the effect of geometrical structure on dissociative chemisorption.

**University of Rochester
Rochester, NY 14627**

Department of Chemistry

**218. Low-Energy Ion-Molecule Reactions and
Chemi-Ionization Kinetics**
Farrar, J.M. **\$86,000**
Comm. 716-275-5834

Crossed ion beam-neutral beam reactive scattering experiments are being performed on several chemical systems with the goal of using energy disposal measurements and angular distributions to deduce dynamical information about reactive collisions and potential surface topology. By studying proton transfer and isotope exchange collisions and nonreactive energy-transfer collisions in systems such as OH⁻ + D₂, OD⁻ + NH₃, and OD⁻ + CH₂=CH=CH₂, the branching ratios yield quantitative information on isomerization barrier heights and the product recoil distributions assess the statistical nature of intramolecular energy transfer in the collision complex. Product state-resolved electron detachment reactions are also being studied in important combustion-related reactions such as O⁻ + H₂ and O⁻ + C₂H₄, as well as atmospheric reactions such as O⁻ + N₂O and O⁻ + CO.

**219. Double Resonance Reactant Preparation
for State-to-State Unimolecular Reaction
Studies**
Rizzo, T.R. **\$129,000**
Comm. 716-275-2304

The unimolecular decomposition of highly vibrationally excited molecules plays an important role in the kinetics of complex systems, and accurate models of the dissociation dynamics are needed for quantitatively predicting overall reaction rates. The goal of this work is to develop and implement new spectroscopic techniques for studying highly vibrationally excited molecules on the ground potential energy surface. The spectroscopy of molecules excited to energies near dissociation provides important information about the dissociation dynamics that can critically test calculated results. This project uses recently developed infrared-optical and optical-infrared double resonance techniques to explore the reaction dynamics of vibrationally excited molecules. Infrared-optical double resonance spectroscopy of H₂O₂ and NH₂OH has elucidated the role of reagent rotational motion in unimolecular reactions, an issue that statistical theories often treat inadequately. Moreover, this approach has provided accurate values for the dissociation energies of these two molecules and has revealed the presence of a barrier in the exit channel of the H₂O₂, potential surface. Optical-infrared double resonance spectroscopy of H₂O₂, HONO₂, and (CH₃)₃COOH has provided a new standard by which

to judge the completeness of intramolecular energy redistribution in highly excited molecules and clearly defines the limits of statistical theories.

**SRI International
Menlo Park, CA 94025**

Molecular Physics Laboratory

**220. Flame Studies, Laser Diagnostics, and
Chemical Kinetics**
Crosley, D.R. **\$37,000**
Comm. 415-859-2395

This research project involves a combination of laser-induced fluorescence (LIF) and chemical kinetics measurements to investigate the kinetics of pollutant formation in hydrocarbon and ammonia combustion processes. The research includes: (1) LIF probing of reactive intermediates in flames at atmospheric and reduced pressure; (2) the development of a spectroscopic and state-specific collisional database for LIF measurements; (3) development and application of rate constant estimation methods; (4) computer modeling of combustion chemistry networks; and (5) rate constant measurements, especially at higher temperature, using a laser pyrolysis/LIF technique. Collisional quenching of very high rotational levels of the A³ π state of NH has been studied by LIF following laser photolysis of ammonia. For NH₃ and CH₄ colliders, the quenching cross sections decrease with rotational level to J = 28, the highest level studied. Reactions for which negative activation energies have been reported and used to determine many critical hydrocarbon bond energies important in combustion are under investigation.

**University of Southern California
Los Angeles, CA 90089-0482**

Department of Chemistry

**221. Combustion-Related Studies Using Weakly
Bonded Complexes**
Beaudet, R.A. **\$90,000**
Comm. 213-740-4125

Binary van der Waals complexes relevant to combustion are being prepared and studied using tunable infrared radiation diode laser spectroscopy. The complexes are prepared in supersonic expansions using pulsed slit nozzles. In the first phase, geometries and other molecular properties are determined from vibration-rotation spectra. In the second phase, these complexes will be used as precursors in photoinitiated reactions. Two classes of binary complexes are being investigated. The first involves molecular oxygen (e.g., O₂-HCN, O₂-HF, O₂-HCl, O₂-HBr, and O₂-hydrocarbons) and corresponding photoinitiated reactions. Such complexes involving triplet state molecules have not yet been studied. These complexes are interesting because upon photodissociating the hydride portion, the reaction of H and O₂ via the vibrationally excited HO₂[†] intermediate can be studied, [e.g., BrH-O₂ + hv(193 nm) → Br-H-O₂ → Br + HO₂[†] → Br + OH + O]. The second thrust area is the study of a unique set of species involving oxygen atoms and small molecules such as HF, HCl,

HBr, HCN, and hydrocarbons. Since the reactions of $O(^3P)$ and small molecules have significant activation energies, the complexes survive in supercooled jets, and the oxygen atom will lie in a shallow well just outside the barrier. $O(^3P)$ has been prepared by the photolysis of SO_2 at 193 nm in the expansion slit.

222. Reactions of Carbon Atoms Using Pulsed Molecular Beams
Reisler, H. **\$81,128**
Comm. 213-740-7071 **(18 months)**

The reaction dynamics of carbon atoms in their ground and first excited states are being studied using crossed pulsed molecular beams. A beam of carbon atoms is prepared by laser ablation of graphite and crosses a free jet containing the second reactant. Products are monitored by LIF, and E,V,R,T product distributions are determined. An example of an elementary reaction that is currently under investigation is the reaction of carbon with nitrous oxide. The CN products, which are observed under nearly single-collision conditions, are produced with an inverted vibrational distribution and a Boltzmann-like, "hot" rotational distribution. In addition, the reactions of $C(^1D)$ (produced via two-photon dissociation of carbon suboxide at 248 nm) with HCl and H_2 are being studied. The E,V,R distributions and Lambda-doublet propensities in the CH products are determined, and the role of the carbene intermediate is investigated. In the reaction with HCl, both CH and CCL are observed as reaction products, with the latter being the more abundant channel. The results are analyzed in terms of an insertion mechanism and carbene intermediates. Endothermic reactions of carbon atoms will be studied with vibrationally excited polyatomic reactants.

223. Reactions of Small Molecular Systems
Wittig, C. **\$95,000**
Comm. 213-740-7368

This research is concerned with detailed aspects of reactions involving small polyatomic systems. Reaction cross sections are obtained from near-threshold to collision energies as high as $21,000\text{ cm}^{-1}$ for reactions of H atoms with N_2O , NO_2 , and O_2 . In addition, product V,R,T excitations are thoroughly mapped throughout the accessible energy ranges. In the past (i.e., $H + CO_2 \rightarrow OH + CO$), these measurements have shown marked variations of reaction cross-section vs collision energy at energies where statistical theories fail and product excitations are known to be nonstatistical. Experiments using velocity-aligned Doppler spectroscopy will exploit the VUV/TOF method. In addition to photodissociation studies (C_2H_2 and HCN), bimolecular reactions are amenable to this technique, and are stressed. Several reactions will be examined that give H atoms: (1) $O(^1D) + H_2 \rightarrow OH + H$ and $F + H_2 \rightarrow HF + H$ will be used to test the machine, (2) $OH + CO \rightarrow CO_2 + H$ where a high-resolution H-atom kinetic energy distribution can yield a complete mapping of CO_2 internal excitation, and (3) $NH(a^1\Delta) + NO \rightarrow N_2O + H$. Further experiments involve stimulated emission pumping of reactants (e.g., $OH + NO \rightarrow H + NO_2$, $\Delta H = 10,200\text{ cm}^{-1}$, where either OH or NO can be pumped to high vibrational levels).

Stanford University
Stanford, CA 94305

Department of Mechanical Engineering

224. Spectroscopy and Kinetics of Combustion Gases at High Temperatures
Hanson, R.K.; Bowman, C.T. **\$135,000**
Comm. 415-723-1745

This research involves two complementary activities: (1) development and application of continuous wave (CW) ring dye laser absorption methods for sensitive detection of radical species and measurement of fundamental spectroscopic parameters and (2) shock tube studies of radical-molecule and radical-radical reactions relevant to combustion. A novel aspect of the shock tube work is the use of excimer laser photolysis to produce controlled levels of radical species in shock-heated gases. Reactions involving H_2 , O_2 , NO , H , N , and O have been studied; source compounds employed for radical production were H_2O , NH_3 , and NO . The primary excimer wavelength utilized for photolysis has been 193 nm (argon fluoride), although other wavelengths are also of interest. Species investigated in the spectroscopic portion of the research include OH, NH, NH_2 , and NO.

State University of New York at Buffalo
Buffalo, NY 14260

Department of Electrical and Computer Engineering

225. Picosecond CO_2 Laser Interactions with Polyatomic Molecules
Kwok, H.-S. **\$76,908**
Comm. 716-636-3119 **(18 months)**

The goal of this project is to study the ultrafast dynamics of excited molecular states. Broadband incoherent light pulses are used to probe various molecules in a dynamic grating type arrangement. In this self-diffraction geometry, the signal is measured as a function of the delay time between the two pump pulses. The time resolution is <10 fs, which is very difficult to achieve with coherent light pulses. So far, the following effects have been observed: (1) molecular vibrational modulation (37 fs) of the self-diffraction signal in R-565 and CV-670 dyes, (2) 1.6 fs Michelson interference fringes in the photodissociation of NO_2 , and (3) ultrafast photodissociation (<40 fs) in NO_2 using 400 nm laser excitation. The ultrafast photodissociation time in NO_2 is quite unexpected because the excess energy above the dissociation limit is quite small. Additionally, dephasing information of the upper level can also be obtained. T_2 times of 20 to 200 fs were observed in various dye molecules. The photodissociation experiment will be extended to other molecules in the future.

State University of New York at Stony Brook
Stony Brook, NY 11794

Department of Chemistry

226. Studies of Atmospheric Molecules by Multiphoton Spectroscopy

Johnson, P.M. **\$83,000**
Comm. 516-632-7912

Resonance ionization spectroscopy is currently being applied to the investigation of the optical transitions and photochemistry of molecules, including metastables, which are difficult to study using conventional techniques. New transitions of both familiar and unstable molecules provide additional information about their excited-state electronic structure and enable the detection of minute quantities in difficult environments. Normally the species under study are entrained in a supersonic beam, providing a collisionless and cold environment. Unstable molecules are created in the supersonic beam by means of a pulsed electric discharge at the exit of a pulsed valve. Current molecules being studied include carbon dioxide and metastable nitrogen. Multilaser, multiphoton techniques, including mass spectroscopy and photoelectron spectroscopy, are being used. A new technique called mass analyzed threshold ionization spectroscopy is being developed that provides high resolution spectra of ionic states with mass discrimination. This will enable the equivalent of photoelectron spectra in environments where more than one species is present and being ionized. In carbon dioxide the selectivity of multiphoton ionization for photochemically stable states enables the discrimination of detailed structure from a continuous background and a better understanding of its electronic structure and photodissociation. Photoelectron spectra show evidence that ionization is taking place during a dissociative displacement. In metastable nitrogen, new transitions between excited states enable a fresh look at some previously obscure electronic states.

University of Wisconsin at Madison
Madison, WI 53706

Department of Chemistry

227. Unimolecular Reaction Dynamics and Vibrational Overtone Spectroscopy of Highly Vibrationally Excited Molecules

Crim, F.F. **\$89,971**
Comm. 608-263-7364

This research is designed to determine the nature of highly vibrationally excited molecules, to probe unimolecular reactions at the level of individual quantum states, and to study the dynamics of electronic photodissociation from vibrationally excited states. In these experiments, pulsed laser excitation of a vibrational overtone transition prepares a highly vibrationally excited molecule and time-resolved spectroscopic detection of products and monitors their subsequent decomposition. This approach (1) provides data on unimolecular reactions of large and small molecules in room-temperature gases and supersonic

expansions and (2) probes the role that vibrational excitation plays in electronic photodissociation dynamics. These latter experiments potentially determine the nature of the initial state prepared by vibrational overtone excitation and reveal unique electronic photodissociation dynamics for vibrationally excited molecules. Measurements of the populations of the product quantum states and the rates of decomposition in vibrational overtone-initiated unimolecular reactions permit detailed comparison with different theoretical models. These studies test statistical theories of unimolecular reactions and provide data on the dynamics of isolated molecules that are useful for understanding combustion processes, atmospheric chemistry, and laser-initiated reactions. Two recent examples of exploiting highly vibrationally excited molecules to achieve unique chemistry are the bond-selected photodissociation and bimolecular reaction of HOD. In these experiments, vibrational excitation of the O-H bond leads to its preferential cleavage.

Atomic Physics

California State University, Fullerton
Fullerton, CA 92634

Department of Physics

228. Correlated Processes in Atomic Collisions

Feagin, J.M. **\$45,983**
Comm. 714-773-3366

Key features of resonances observed in H⁻ photoionization experiments and calculated in detail by various computational methods have been explained in a very simple way using a description of two-electron atoms based on the hydrogen molecular ion. The coordinate plane in which the molecular H₂⁺ Schrödinger equation separates is mapped onto plots of the computed two-electron probability densities. The mapping clearly shows that nodal lines characterizing the resonances are described by fixed values of a particular molecular coordinate as the other coordinates are varied. This identification of molecular nodes leads directly to a set of propensity rules that predict and account for intensities of the observed resonances. In another project, a theory of ion-atom resonant transfer with excitation (RTE) has been adapted to calculate measured cross sections for fast ions traveling along a gold channel. A tight-binding model of the gold lattice is introduced to represent the crystal's periodicity, and the RTE cross section is proportional to an atomic Compton profile multiplied by a crystal-structure factor. This explains the exceedingly narrow RTE widths that have been observed. Additional recent efforts have concentrated on the calculation of Wannier threshold laws for three- and four-electron escape to compare with new experimental measurements being made in several European laboratories. Multiple Wannier power laws have been predicted that are in accord with independent experimental observations. Of fundamental interest is the energy dependence of cross sections for single and multiple ionization of atoms by positron impact, experiments that could be performed in this country using merged relativistic beams.

Clark Atlanta University
Atlanta, GA 30314

Department of Physics

229. Theoretical Investigation of Electron-Ion Interaction

Msezane, A.Z. **\$87,000**
Comm. 404-880-8662 **(14 months)**

Dominant physical mechanisms underlying the processes of photoionization and electron-impact excitation and ionization of ions and atoms of importance in astrophysical, laser, and laboratory fusion plasmas are identified and calculated. Extensive configuration interaction target wave functions, which take into account correlation and polarization effects, are used in the R-matrix method and program NIEM of Henry et al. to obtain both differential and integral cross sections to guide measurements. In particular, detailed multistate photoionization calculations are performed of: (1) ground state atoms to investigate the recently predicted strong satellite enhancement of the single-channel cross sections in sodium and potassium and to delineate the accompanying resonance structure and (2) excited states from inner shell to investigate and understand the recent experimental measurement of strong enhancement of shake-up satellites and many-electron effects in sodium. Also, electron-impact excitation is studied from near threshold to about ten times threshold of core-excited atomic quartet and doublet states, particularly those quartet states that are metastable against autoionization (e.g., Na I), of atoms, and singly and multiply charged positive ions to investigate target wave function effects and scattering approximations.

University of Colorado
Boulder, CO 80309-0440

Joint Institute for Laboratory Astrophysics

230. Near-Resonant Absorption by Atoms in Intense Fluctuating Fields

Smith, S.J. **\$105,000**
Comm. 303-492-7788

This program has focused on an experimental investigation of the behavior of atoms coherently excited by a near-resonant, very intense laser field, on which statistically well-characterized and well-controlled phase/frequency fluctuations have been imposed. A comprehensive experimental investigation of the variance of the fluorescence intensity fluctuations and the spectra of these fluctuations, from a two-level atom pumped by a phase-diffusing laser is now completed. Excellent agreement with recently developed theoretical predictions relating the observed quantities to the laser field parameters is obtained. An area of current interest is the influence of a phase-diffusing field on four-wave-mixing (FWM) in diffuse media. An experiment to investigate the effects of time-delayed pump and probe beams on the FWM signal from a two-level system is currently in the advanced planning stage. A related theoretical investigation of this problem was recently completed. Another experiment currently under way is to study the effect of an amplitude-modulated, phase-diffusing optical field on

the Hanle signal from a three-level system. Phase sensitive detection of the signal is expected to reveal qualitatively different behavior depending on whether the laser is monochromatic or broadband.

Department of Physics

231. Physics of Correlated Systems

Greene, C.H. **\$95,000**
Comm. 303-492-4770 **(15 months)**

A variety of atomic systems displaying correlations or nonseparable quantum behavior will be investigated theoretically. A major effort will be undertaken to find the most efficient theoretical description of open-shell atomic systems, emphasizing atoms heavier than argon, and including the transition metals and their negative ions. The possibility of a nearly *ab initio* multichannel quantum defect description of these complex systems will be investigated, making use of recent rapid progress in understanding electron correlations in atoms with a few valence electrons. New general methods will be investigated and detailed calculations will be performed for selected prototype systems. A second effort will attempt to describe the behavior of a hydrogen atom in a strong laboratory magnetic field in the energy range near and above the ionization threshold. A combination of frame transformation and variational methods with quantum defect theory, which can explain features observed in the quasi-Landau spectrum, will be used to solve this nonseparable quantum mechanics problem. Investigation of particle-particle correlations in comparatively simple few body atomic systems, such as H^{-} , Ps_2 , and highly doubly excited states of He and H^{-} approaching the Wannier threshold region is a third part of this project. For these systems hyperspherical coordinate methods will be used to sort out the qualitative dynamical features such as the major decay pathways, as well as to identify quantitative resonance energies in these systems.

Cornell University
Ithaca, NY 14853

Nuclear Science and Engineering Program

232. Experimental Study of Interactions of Highly Charged Ions with Atoms at keV Energies

Kostroun, V.O. **\$293,304**
Comm. 607-255-4991

The goal of this experimental project is to investigate fundamental processes that occur in low-energy, very highly charged ion-atom (ion) interactions at kinetic energies typical of thermonuclear plasmas. Processes being studied include single, double, and multiple electron capture by the projectile, transfer ionization, formation of quasi-molecules in collisions, excitation and ionization of the target, and decay of highly excited states of the projectile formed in capture. Low-energy (<1 keV/amu), multiply charged ions ($q \geq 8$), are crossed with gas targets, and the reactions studied by several techniques, including recoil ion spectroscopy, recently made practicable in this laboratory. During the past year, absolute total, and one and two electron transfer cross sections for 28 keV Ar^{4+} ions, ($8 \leq q \leq 14$) in molecular hydrogen and helium have been

measured with an error of 10%, a factor of 2 to 3 better than typical measurements of such quantities. The highly charged ions are produced by the Cornell Electron Beam Ion Source (CEBIS), a superconducting solenoid, cryogenic EBIS, designed and constructed in this laboratory. CEBIS produces such species by sequential electron impact ionization of ions trapped in an energetic, high-current-density electron beam.

**Georgia Institute of Technology
Atlanta, GA 30332-0430**

School of Physics

233. Statistical Fluctuations in Lasers
Roy, R. **\$74,212**
Comm. 404-894-5265

Studies on statistical fluctuations in dye lasers have led to new realistic models for the simulation of statistical fluctuations in lasers interacting with atoms and molecules. It is necessary to include laser phase and amplitude fluctuations in models of atom-field interactions to determine dephasing times for atoms by spectroscopy with time-delayed incoherent fields (as opposed to ultrashort pulses). Four-wave mixing between the pump and probe fields with fluctuations on arbitrary time scales have been studied. The effect of four-wave mixing between two strong pump fields at distinct frequencies propagating in an optical fiber has also been studied both theoretically and experimentally. The optical energy of the pump waves is redistributed into sidebands generated within the fiber because of four-wave mixing. The exchange of energy between pump waves and sidebands has been shown to be periodic or chaotic, depending on the strength and detuning of the waves. A novel source of broadband incoherent radiation is under preparation in the laboratory. A tunable titanium doped sapphire laser with an intracavity acousto-optic frequency shifter will be used to generate tunable radiation with gigaHertz bandwidths. Such a source may find applications in laser cooling of atomic and molecular beams.

234. Metastable Enhancement of C⁺ and O⁺ Capture Reactions
Thomas, E.W. **\$17,985**
Comm. 404-894-5200

Low-energy (10 to 500 eV) metastable C and O ions exhibit charge transfer cross sections in H₂ ten times greater than the ground state. This can be related to an accidental resonance of these metastable states with vibrationally excited H₂⁺. This observation suggests ion beams used in other experiments contain indeterminate fractions in the metastable state and accounts for discrepancies in reported data. The charge transfer of C⁺ and O⁺ in atomic H is being studied. It is anticipated that a high cross section will be found for ground state oxygen ions in hydrogen associated with the presence of an accidental resonance. Cross sections for ground state species and for metastable carbon ions are expected to be smaller because of a large energy defect. The results have implications for the understanding of how carbon and oxygen impurity ions are neutralized at the edge of a fusion plasma.

**Harvard University
Cambridge, MA 02138**

Harvard-Smithsonian Center for Astrophysics

235. Theoretical Studies of Highly Ionized Species
Dalgarno, A. **\$138,000**
Comm. 617-495-4403

Potential energy curves of HCl⁺ have been determined and the cross sections for charge transfer of protons in collisions with neutral chlorine atoms are being calculated. The possibility that the cation NHe²⁺ may have long-lived quasi-bound states is being explored. Collisions at ultralow temperatures have many interesting features arising from their sensitivity to weak perturbations at large distances. These features will be investigated and, in particular, spin-change collisions of alkali metals will be examined quantitatively. Time-dependent studies offer new insights into collision phenomena and will be studied.

**Kansas State University
Manhattan, KS 66506**

Department of Physics

236. Atomic Physics of Strongly Correlated Systems
Lin, C.D. **\$130,000**
Comm. 913-532-6786

This project is directed at the understanding of the formation and the decay properties of multiply excited states of atoms and ions. The ejected electron spectra from autoionized states formed by double electron capture in the collision of multiply charged ions with atoms are analyzed theoretically and the results are compared with experiments. The effects of interference among different doubly excited states and the post collision interactions are studied. Electron capture cross sections from laser-excited target atoms are being studied and the alignment and orientation parameters of excited states populated in collisions are investigated using quantal and classical theories. The properties of Coulombic three-body systems of arbitrary masses are examined using mass-weighted hyperspherical coordinates to provide a unified treatment of atoms and molecules.

237. Atomic Physics with Highly Charged Ions
Richard, P. **\$1,545,000**
Comm. 913-532-6783

The KSU electron beam ion source (EBIS) facility has been used to measure dielectronic recombination on and electron-impact excitation of heliumlike argon and dielectronic recombination on heliumlike neon. New EBIS experiments studying the effects of low velocity, highly-charged argon ions on surfaces and energy loss in thin foils have been initiated. Auger electron spectroscopy from ion-atom collisions continues to be used to study binary encounter electron production, resonance transfer and excitation, and projectile ls ionization and ls → 2p excitation because of the electron-electron interaction. Theoretical

calculations have demonstrated that the observed enhanced 0° (in the lab) binary encounter electron cross section for few electron ions over bare ions is because of the 180° electron scattering from the static charge of the projectile ion. It has also been demonstrated that electron exchange in 180° scattering contributes to the observed effect. Experiments have recently been undertaken to study the quantum beats of Rydberg atoms field ionized in a Rydberg analyzer. The angular distribution of electron capture from D_2 by O^{8+} has been studied further by an improved experimental apparatus. The data showed the capture cross section for this collision system is peaked at the alignment angle of 90° with respect to the beam axis, which is qualitatively in agreement with the theories. The measurement of the angular distribution of recoil ions created in bare ion-atom collisions has continued with much success. The velocity distribution of recoil ions shows a clear evolution from quasi-spherical, for soft collisions, to a ring perpendicular to the beam in the case of hard collisions. The theoretical efforts consist of calculations of the variation of resonance strengths with n for dielectronic recombination in heliumlike ions, the satellite spectra for high-lying resonance states of heliumlike chromium and nickel, and the satellite line intensity factors for dielectronic satellites of Li-like ions. Calculations of the density matrix of $H(n = 2,3)$ states formed in p -He collisions have been completed as well as calculations of two-electron transitions in $Z^{q+} + He$ collisions and state-selective double capture to doubly excited states at low collision velocities. Calculations of projectile electron loss with molecular hydrogen targets and projectile ionization by molecular hydrogen-orientation dependence have been performed to compare with recent experiments.

University of Louisville Louisville, KY 40292

Department of Physics

238. Spectroscopic Studies of Hydrogen Collisions

Kielkopf, J. **\$78,000**
Comm. 502-588-6787

Low-energy collisions involving neutral excited states of hydrogen are being studied with vacuum ultraviolet laser spectroscopy. Atomic hydrogen is generated by focusing an energetic pulse of ArF, KrF, or YAG laser light onto molecular hydrogen to make a small plasma localized near the focal point. The H_2 molecules within this volume are dissociated by the initial heating, and by the ionization and dissociative recombination that occur during and shortly after the laser pulse. After a short delay, the cooling atomic hydrogen gas is probed by tuned lasers, including vacuum ultraviolet light generated by four-wave mixing in Hg vapor. The work includes a study of the Lyman α profile caused by neutral collisions, with an emphasis on densities greater than 10^{19}cm^{-3} . Other experiments that are part of this program are investigating the bound-free continua in H_2 and OH in a study of $H + H$ and $H + O$ collisions, the population inversion that occurs in $Al + H_2$ with ArF (193 nm) excitation, and line profiles and intensities in a study of excited-state collision processes for such systems as $Na + H$.

National Institute of Standards and Technology, Gaithersburg Gaithersburg, MD 20899

Physics Laboratory

239. Electron-Atom Collision Studies

Kelley, M.H.; McClelland, J.J. **\$89,500**
Comm. 301-975-3722

Crossed-beam scattering experiments are carried out using low-energy spin-polarized incident electrons and optically pumped atoms. Laser-optical pumping of the target atoms prepares either spin-polarized ground state atoms, or spin-polarized, aligned, and/or oriented excited-state atoms. Electrons scattered from the optically pumped atoms are detected as a function of scattering angle, incident energy, and relative spin orientation. These experiments are designed for fundamental tests of the reliability of theoretical electron scattering calculations, with particular emphasis on the role played by exchange. Sodium has been the major focus of this work to date, since with its single valence electron, it provides a good model system for investigation of exchange in electron-atom scattering. In future experiments, spin-polarized electron scattering from optically pumped chromium atoms will be investigated. In chromium, because the incident spin-polarized electron has the opportunity to exchange with each of the six target valence electrons, a wide and complex range of exchange phenomena can be expected.

University of Nebraska Lincoln, NE 68588-0430

Department of Physics and Astronomy

240. Dynamics of Collision Processes

Starace, A.F. **\$63,100**
Comm. 402-472-2795

This project is concerned with collision processes that are governed by the dynamics of three interacting charged particles. Results in two broad areas have been obtained over the most recent project period. First, detailed theoretical analyses have been presented of the projectile energy dependence as well as the target dependence of the electron detachment collision processes, $H^- + T \rightarrow H(n = 1,2) + T^* + e^-$, for targets $T = He, Ne, Ar, Kr,$ and Xe , and for incident H^- projectile energies of 0.1, 0.5, 1.0, and 1.5 MeV. Inclusion of $H(n = 2)$ final states in the calculations gives marked improvement in the agreement of theory with experimental data. Second, a large number of processes involving laser-induced detachment of H^- have been studied, i.e., $N\gamma + H^- \rightarrow H(n = 1,2) + e^-$, where $N = 1,2,3$. The use of adiabatic hyperspherical wave functions provides in many cases the most detailed treatment of electron correlation effects to date. Particularly noteworthy, for 2-photon detachment of H^- with excitation of $H(n = 2)$, is identification of a half-cycle of long-range dipole-field-induced oscillation of the cross section above threshold. Such oscillations have never been observed experimentally.

University of Nevada
Reno, NV 89557-0020

Department of Chemistry

241. Screening Resonances in Plasmas
Winkler, P. **\$42,156**
Comm. 702-784-6792

In the investigation of plasmas consisting of positive atomic ions and electrons a good understanding of the interaction potential between those two species is essential. Compared to the vacuum case the force between the charges is modified because of short-range order and dynamical screening effects introduced by neighboring ions and fast electrons, respectively. These modifications determine one-electron properties (e.g., spectral lines that serve as key quantities in plasma diagnostics) as well as more-electron properties (e.g., dielectronic recombination rates that account for plasma losses). As a first step beyond the usual Debye-Hückel treatment of screening, realistic electron-ion potentials were derived from pair distribution function calculations and examined for the occurrence of low-lying scattering resonances in the s-wave channel. In all cases studied, such resonances were found. Enhanced recombination rates are being calculated. The required computational techniques have been developed and tested using analytic model potentials. The incorporation of the realistic electron-ion potentials into the calculation of various ionic pair functions is under way.

University of New Mexico
Albuquerque, NM 87131

Department of Physics and Astronomy

242. Relativistic Atomic Beam Spectroscopy II
Bryant, H.C. **\$121,500**
Comm. 505-277-3044

The spectroscopy of H^- , important to fusion research, astrophysics, and accelerator physics is studied at Los Alamos Meson Physics Facility (LAMPF). The techniques developed for relativistic beams are currently being applied to study multiphoton processes in this negative ion. Using a high-power carbon dioxide laser, photons in the 10.6 micron line are Doppler-shifted to energies in the ion's rest frame ranging from 34 to 400 MeV allowing study of multiphoton electron detachment involving 2 to 22 photons at a beam energy of 800 MeV. The simplicity of the system under study, combined with the effective tunability of a high-intensity laser, makes these measurements unique. Another study concerns how the high-lying, doubly excited states in the negative hydrogen ion undergo double detachment. Current results indicate that so-called "ridge-states," which may be related to the Wannier double detachment mechanism, are being observed. An extensive survey of the systematics of these states is planned. Further studies of electric field effects and passage through foils on the stability of H^- are also planned.

University of Oregon
Eugene, OR 97403

Department of Physics

243. Nonlinear Dynamics of Broad-Band Lasers
Raymer, M.G.
Comm. 503-346-4785

The dynamical behavior of lasers operating simultaneously in many longitudinal modes is being studied experimentally. Significant progress has been made in determining the origin of the apparently random fluctuations in the amplitudes of the lasing cavity modes in a continuous dye laser. It was found that coherent four-wave mixing in the gain medium continually couples energy from one mode into another and a steady state is never reached. Current work is directed toward understanding the influence of quantum mechanical noise (spontaneous emission) on the laser dynamics very near, but just above, the lasing threshold, where such effects are predicted to be significant. These studies will be carried out with titanium-sapphire lasers, recently developed room-temperature, solid-state lasers that are tunable in the visible, and with dye lasers. The longer upper-level lifetime in the titanium-sapphire compared to the dye laser will change the nature of the dynamics. Relaxation oscillations caused by level-population dynamics may have to be taken into account. These studies have potential to help in the understanding of intracavity laser spectroscopy, an extremely sensitive technique for detecting low-concentration species.

Pennsylvania State University,
Lehman
Lehman, PA 18627

Department of Physics

244. Electron Transfer, Ionization, and Excitation in Atomic Collisions
Winter, T.G.; Alston, S.G. **\$66,000**
Comm. 717-675-9278

Cross sections are calculated for the processes of electron transfer, excitation, and ionization in ion-atom collisions at keV to MeV energies. One- or two-electron systems are considered, since approximations can be controlled better. At the lower-energies, where the probability of electron transfer is largest, coupled-state approaches are applied because of the strong coupling of many states. Earlier one-electron work using large coupled-Sturmian-state bases is extended to the two-electron proton-helium-atom system at intermediate energies. Other work at high energies has explored the influence of single-ionization channels on the excitation of the lowest doubly-excited state of helium. At higher energies where perturbative approaches become applicable, recent work has centered extending the second-order Faddeev approximation for charge transfer to ion-ion collisions since the residual intrasystem Coulomb interaction requires the use of distorted-wave scattering states. Another approach, the strong-potential approximation, is applicable for charge asymmetric collisions; a comparison of numerical results of this method

with those of the coupled-state approach is under way to obtain a connection between the two methods. Finally, a study of simultaneous charge transfer and projectile excitation in asymmetric collisions using perturbative techniques is in progress.

University of Pittsburgh Pittsburgh, PA 15260

Department of Physics and Astronomy

245. *New Infrared Photon Absorption Processes*

Bayfield, J.E. **\$120,000**
Comm. 412-624-9280

The simultaneous application of resonant ultraviolet and nonresonant mid-infrared laser radiation is a possible approach for the spatially localized subpicosecond noncollisional breakdown of gases. Fast atomic beam experiments are being carried out on the carbon dioxide infrared laser multiphoton ionization of optically excited hydrogen atoms in selected Stark states, with principal quantum numbers selected between $n = 5$ to 10. At present, infrared laser intensities of 1 Gigawatt per square centimeter and subnanosecond laser pulse lengths are being used. At $n = 10$ the peak laser pulse strength is seven times the static field strength needed for rapid ionization. At $n = 5$ the initial Rabi frequency is one quarter the laser frequency which in turn is one half the initial electron orbit frequency; then the laser field strength is equal to the threshold value for classically chaotic ionization. Both of these strong-field regimes are previously unstudied at infrared wavelengths and may feature infrared laser ionization rates enhanced over perturbative values. The study of hydrogen atoms in extremal Stark states makes it possible to estimate accurate quantum and classical ionization rates. The development of a numerical capability in support of the experimental program was started.

Rice University Houston, TX 77005

Department of Physics

246. *Theoretical Atomic and Molecular Physics*

Lane, N.F.
Comm. 713-527-4026

Theoretical methods, based on quantum mechanical and semiclassical approaches, have been applied to the calculation of cross sections and other observables for various atomic collision processes that are of fundamental interest and important to advanced energy research. Recent progress includes results for (1) quenching of Rydberg alkali atoms in slow collisions with rare-gas atoms; (2) state-selective excitation in electron-capture collisions between highly stripped ions (e.g., C^{4+}) at keV energies and alkali atoms, as well as H_2 molecules; (3) differential direct elastic scattering and single and double charge transfer in collisions between He^{5+} and He atoms at keV/amu energies; and (4) very low-energy (MeV) quasi-resonant charge-transfer collisions between $^3He^+$ and 4He and between $^4He^+$ and 3He . Research is continuing on

similar processes and on new theoretical and computational methods.

University of Rochester Rochester, NY 14627

Department of Physics and Astronomy

247. *Multiphoton Processes in Intense Photon Fields*

Eberly, J.H.; Meyerhofer, D.D. **\$132,000**
Comm. 716-275-3288 **(15 months)**

High-intensity laser-atom interactions are studied both theoretically and experimentally. The principal experimental tool will be the table Top Terawatt (T^3) laser. The relationship between the tunneling or barrier suppression regime observed in experiments and the multiphoton regime observed with different laser wavelengths, pulse shapes, and/or pulse widths are studied by varying laser pulse width and bandwidth independently. The characteristics of photoionization will be studied. Theoretical investigations will continue using *ab initio* wave functions calculated for representative model atoms. This approach has proven fruitful in the examination of above threshold ionization (ATI) phenomenology, including a test of KFR theory, observation of giant Stark shifts, mapping of bound states onto ATI electron peaks, high-order harmonics in light scattering and plateau phenomena, and the correlation of high-order harmonic spectra with ATI electron spectra. The principal focal areas for new work will be the improvement of numerical methodology and the study of atom stabilization under strong radiation fields. The theoretical effort will lead naturally to support of experimental work as well.

University of Tennessee Knoxville, TN 37996-1200

Department of Physics and Astronomy

248. *Production and Destruction of Metastable Negative Ions*

Pegg, D.J. **\$86,000**
Comm. 615-974-7831

This project involves an experimental study of photon-negative ion interactions using a crossed laser-ion beam apparatus. Forward-directed photoelectrons from the interaction region are energy analyzed using a spherical-sector electron spectrometer. The resulting spectra provide information on the kinetic energies and yields of the ejected photoelectrons. Their angular distributions can be measured by rotating the linear polarization vector of the laser beam. The negative ion of Ca has been found to be, contrary to earlier expectations, stably bound in the $4s^2 4p^2 P$ state (electron affinity of 43 MeV). Partial cross sections for detaching either the 2s or the 2p electron from the metastable $He^-(1s2s2p^4P)$ ion have been determined at several different photon energies in the visible. Measurements of cross sections for photodetaching Li^- and B^- ions are under way. A recent measurement of the Li^- photodetachment cross section at $\lambda = 662.7$ nm was found to be in good agreement with theory.

**Texas A & M University
College Station, TX 77843**

Cyclotron Institute

- 249. Excitation of Atoms and Molecules in Collisions with Highly Charged Ions**
Watson, R.L. **\$86,000**
Comm. 409-845-1411

Experiments have been performed to examine the yield and kinetic energy distributions associated with the different charge division pathways for the dissociation of multicharged O₂, N₂, and CO molecular ions produced by fast heavy ion impact. A beam of 96 MeV Ar¹⁴⁺ ions was directed through a differentially pumped gas cell containing the molecules of interest into a microchannel plate detector. Dissociation products produced in ionizing collisions were accelerated out of the gas cell by an electric field into a time-of-flight spectrometer. By employing two-parameter coincidence techniques, the times of flight of first-arrival fragments and the time difference distributions for binary pairs were recorded on magnetic tape event-by-event so as to maintain their correlation. Transformation of the time difference distributions into kinetic energy distributions required a detailed simulation of the ion trajectories in order to construct the response matrix of the spectrometer system. A Monte Carlo procedure was developed for this purpose. The kinetic energy distributions were then extracted from the calculated response matrix and the measured time difference distribution using the Scofield iterative technique. In the case of CO, average kinetic energies and relative yields have been determined for all charge division pairs from C¹⁺/O¹⁺ through C⁴⁺/O³⁺.

**University of Texas at Austin
Austin, TX 78712-1081**

Department of Physics

- 250. Kinetic Studies Following State-Selective Laser Excitation**
Keto, J.W. **\$108,000**
Comm. 512-471-5029

Electronic energy transfer from xenon and krypton atoms is studied following selective excitation by multiphoton laser excitation. During the past year, measurements of state-to-state energy transfer cross sections and radiative lifetimes for Xe*(6p,6p',7p) and Kr*(5p) states in xenon and krypton buffer gases were made. These results are relevant to kinetic models of both excimer lasers and the infrared xenon laser; and they are a significant improvement in the precision of the known radiative lifetimes. The state-to-state rates to specific product channels are determined both from their fluorescent intensity and from the time dependence of fluorescence from the product channel. All product states are studied that can be observed in the spectral range from 120 nm to 1100 nm. Significant amounts of excitation transfer from Xe* to Kr* and return are observed in the energy pathways. The completion of these measurements now enabled the study of termolecular harpooning reactions between Xe* and Cl₂ in krypton buffers. Previously, a large termolecular rate was

observed in xenon buffers but not in argon buffers. A model has been developed that agrees with both sets of experiments and assumes that a collision between the excited state and a buffer atom transiently lowers the ionization potential of the excited state, thereby increasing the harpoon reaction rate. The model predicts a rate for krypton buffers intermediate to that of xenon and argon.

**University of Toledo
Toledo, OH 43606**

Department of Physics and Astronomy

- 251. Semiempirical Studies of Atomic Structure**
Curtis, L.J. **\$55,000**
Comm. 419-537-2341

The project combines programs of experimental measurement, theoretical computation, and phenomenological modeling to precisely specify atomic energy levels, transition probabilities, ionization potentials, polarizabilities, and other spectroscopic properties of highly ionized many-electron atoms. Measurements are made through the use of fast ion beam excitation methods, which are combined with recent data from laser- and tokamak-produced plasmas, astrophysical sources, and conventional light sources. The experimental studies are supported by *ab initio* calculations using the MFE Cray X-MP computer, and predictive semiempirical parameterizations along isoelectronic, homologous, isoionic, Rydberg, and yrast series. Studies conducted during this past year include (1) formulation of a new data reduction that combines energy level and lifetime measurements to form a linearized effective intermediate coupling line strength. Reliable predictions have been made for the resonance and intercombination lifetimes of all stable ions in the Be, Mg, Zn, and Ne isoelectronic sequences. (2) New methods have been developed to experimentally specify intermediate coupling effects on transition probabilities in configurations such as np², np³, and np⁴ which have permitted calculations of M1 rates in the Si, N, P, and S sequences. (3) Precision measurements of hyperfine quenching effects in forbidden transitions of highly ionized members of the helium sequence have also been performed.

- 252. Measurements of Scattering Processes in Negative Ion-Atom Collisions**
Kvale, T.J. **\$86,506**
Comm. 419-537-2980

An experimental study of intermediate energy (10 to 100 keV) collisions between H⁻ ions and target atoms of He, Ne, Ar, and atomic hydrogen is in progress. The method of energy-loss spectroscopy will be used to identify target inelastic processes. An analysis of the spectra will result in the total cross sections for target excitation and ionization being obtained for the above collisional systems. Total cross sections for electron detachment will also be measured and compared to previous values. These experimental measurements will provide stringent tests of theoretical models of fundamental negative ion-atom collisional systems, which will aid in understanding the physics of these collisional systems. This research is being conducted on the UT-Negative Ion Energy-Loss Spectrometer at the University of Toledo.

Vanderbilt University
Nashville, TN 37235

Department of Computer Science

253. Theoretical Studies of Atomic Transitions
Fischer, C.F. **\$130,000**
Comm. 615-322-2926

Atomic structure calculations are being performed to predict properties such as energy levels, binding energies, and lifetimes of excited states. Accurate computational procedures are being devised (1) to predict properties even when they cannot be obtained from experiment and (2) to assist in the identification of observed data. The multiconfiguration Hartree-Fock (MCHF) method, optionally corrected for relativistic effects in the Breit-Pauli approximation, is used in this work. Recent calculations have concentrated on core-excited states of sodium-like ions in order to assist the identification of lines observed in beam-foil spectra. Of primary interest are the quartet levels in the 2500 to 4000 Å region. Both wavelengths and lifetimes need to be predicted. Because of spin-orbit interaction, autoionization is a possible mode of decay as well as radiative transitions. Lifetimes of the $n\text{sp}^2\ ^4\text{P}$ autoionizing states in Be^- , Mg^- , and Ca^- have also been predicted with a view toward explaining why only the first has been observed experimentally. Another problem being investigated is the role of core-polarization in negative calcium. *Ab initio* calculations are difficult and lengthy so a semi-empirical core-polarization approach is being used. Also under development is a modification to the multiconfiguration Dirac-Fock code (GRASP), replacing the full matrix representation by a sparse one. The latter should make possible large relativistic calculations for some levels in Gd with a half-filled f-shell, and the study of correlation in U^{+4} .

University of Virginia
Charlottesville, VA 22901

Department of Physics

254. Studies of Autoionizing States Relevant to Dielectronic Recombination
Gallagher, T.F. **\$107,326**
Comm. 804-924-6817

An important recombination process of impurity ions with electrons in a plasma is dielectronic recombination, in which the electron is first captured into a doubly excited autoionizing state and subsequently decays radiatively to a bound state, completing the recombination process. This research program is focused on the study of the inverse process, the decay of autoionizing atomic states to form an ion and a free electron. The approach employed is laser excitation of the autoionizing states, followed by detection of the resulting ions and electrons. Measurements of the angular distributions of the electrons ejected from Mg 3pns autoionizing states have just been completed. The results of these experiments provide a strict test of theoretical calculations and can be compared to controlled dielectronic recombination measurements. Comparison of the experimental results to theoretical predictions from K

matrix calculations are under way, as are preparations for analogous measurements on the aligned Mg 3pnd states.

Western Michigan University
Kalamazoo, MI 49008-5151

Department of Physics

255. Correlated Charge-Changing Ion-Atom Collisions
Tanis, J.A.; Bernstein, E.M. **\$90,300**
Comm. 616-387-4941

Experimental studies of fundamental atomic interactions involving excitation, ionization, charge transfer, and combinations of these processes are conducted for collisions of few-electron ions with gas targets, crystal targets, or electrons. A major emphasis of this research is the study of two-electron interactions, and particularly those in which the electron-electron interaction plays a role. Specific interaction mechanisms are isolated and identified by detecting charge-changed projectile ions emerging from the collision region in coincidence with X rays, recoiling target ions, or electrons. The studies typically involve ions with $2 \leq Z \leq 92$ in charge states $q \geq Z/2$ and energies ranging from less than 5 keV/u to more than 100 MeV/u. Accelerator facilities at Lawrence Berkeley Laboratory, Argonne National Laboratory, Western Michigan University, and Indiana University are used in this work. Principal areas of investigation are: (1) resonant recombination in ion-atom and ion-electron collisions, (2) double ionization mechanisms in helium at intermediate to high velocities, and (3) two-electron processes leading to continuum electron capture.

The College of William and Mary
Williamsburg, VA 23185

Department of Physics

256. Collisional Detachment of Negative Ions
Champion, R.L.; Dover-spike, L.D. **\$100,000**
Comm. 804-221-3510

The goal of this research project is to develop an understanding of the dynamics of atomic and molecular collisions for systems involving negative ions. The experimental studies are designed to investigate gas-phase, two-body collisions for energies that range from a few electron volts up to several hundred electron volts. These experiments include measurements of total and differential cross sections for a number of exit channels. Mechanisms under investigation include collisional and associative detachment, charge transfer, and ion-molecule reactions. Systems currently being studied include the negative ions of sulfur, oxygen, and several alkali anions in collisions with atomic hydrogen and deuterium. A separate study of negative ion emission from surfaces that are impacted with alkali positive ions is also under way. In this latter experiment, it is observed that a variety of negative ions desorb from a metallic surface with a yield as high as that for sputtering. The mechanism that drives this phenomenon is being examined.

Chemical Energy

Auburn University
Auburn, AL 36849-5128

Department of Chemical Engineering

257. Carbon Deposition and Deactivation of Metallic Catalysts

Baker, T.K.

\$119,973

Comm. 205-844-2007

A combination of controlled atmosphere electron microscopy, *in situ* electron diffraction, and flow reactor techniques is being used to investigate deactivation phenomena associated with supported metal particles. Changes in the behavior of the metal are monitored by the use of probe reactions that are sensitive to the chemical nature of the catalyst surface. These include, graphite gasification in oxygen and hydrogen, and carbon deposition from decomposition of selected hydrocarbons. In studies where platinum was mixed with cobalt the subsequent gasification activity of the bimetallic system in oxygen was found to be inferior to that exhibited by either of the single components. *In situ* electron diffraction analysis shows that there are major differences in the chemical states of the three systems. At temperatures in excess of 350°C platinum is present as discrete metallic particles and attacks the graphite by a channeling mode. A more complex pattern of behavior is observed with cobalt where the oxidation state of the catalyst varies as a function of temperature: CoO (475 to 640°C), Co₃O₄ (665 to 880°C) and Co (>880°C). In the oxide states the catalyst tends to wet and spread along the graphite edges in the form of a thin film and catalyzes the gasification reaction by the edge recession mode. At the high temperature, particles reform and in the metallic state the catalyst proceeds to operate by a channeling action. When platinum-cobalt/graphite specimens are heated in oxygen, then the particles undergo a spreading action on the graphite edges and proceed to attack by the edge recession mode over the whole temperature range, but at a considerably slower rate than that found for the single component systems. *In situ* electron diffraction analysis at 900°C showed that the bimetallic film was present as a mixture of Co₃O₄, Pt₃Co, and Pt. It is possible that cobalt in the oxide form tends to segregate to the gas interface leaving a platinum rich phase in contact with the graphite. These studies are providing new insights into the manner by which additives can modify the interfacial characteristics of a metal, and also influence its catalytic activity.

California Institute of Technology
Pasadena, CA 91125

Department of Chemistry

258. Synthetic and Mechanistic Investigations of Olefin Polymerization Catalyzed by Early Transition Metal Compounds

Bercaw, J.E.

\$133,110

Comm. 818-356-6577

The research program involves studies of Ziegler-Natta olefin polymerizations based on organoscandium and organoyttrium catalysts. The permethylscandocene system, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScCH}_2\text{CH}_2\text{R}$, is sufficiently well behaved to allow studies of the kinetics and mechanism of propagation and chain transfer by β H elimination and of the polymers obtained by "living" ethylene polymerizations, while linked scandocene derivatives, (e.g., $\{(\eta^5\text{-C}_5\text{Me}_4)_2\text{SiMe}_2\}\text{Sc}(\text{H})\text{PMe}_3$ and $[\{(\eta^5\text{-C}_5\text{H}_3\text{CMe}_3)_2\text{SiMe}_2\}\text{ScH}]_2$) promote the head-to-tail dimerization of α olefins, the cyclization of α,ω -diolefins to methylene cycloalkanes and the reversible olefin insertion into Sc-C bonds/ β alkyl elimination to catalyze skeletal rearrangements of 1,4-pentadienes. Synthetic routes to scandium hydride and alkyls having a linked cyclopentadienyl-amide ligand, $\{(\eta^5\text{-C}_5\text{Me}_4)\text{SiMe}_2(\eta^1\text{-NCMe}_3)\}\text{Sc-R}$, also have been developed. These are the most active single component α olefin oligomerization/polymerization systems yet prepared. Evidence for α "agostic" assistance in the carbon-carbon bond forming step for hydro-cyclization of 1,5-hexadiene to methylcyclopentane catalyzed by $\{(\eta^5\text{-C}_5\text{Me}_4)_2\text{SiMe}_2\}\text{Sc}(\text{H})\text{PMe}_3$ has been obtained. Presently under investigation are the syntheses of scandium and yttrium catalysts with ligands having larger and sterically more discriminating ligands, (e.g., $\{(\eta^5\text{-fluorenyl})\text{SiMe}_2(\eta^1\text{-NCMe}_3)\}\text{Sc-R}$, $\{(\eta^5\text{-C}_5\text{H}_2(\text{CMe}_3)_2)\text{SiMe}_2(\eta^1\text{-NCMe}_3)\}\text{Sc-R}$ and $\{(\eta^5\text{-C}_5\text{H}_2(\text{CMe}_3)_2)_2\text{SiMe}_2\}\text{M-R}$ (M = Sc, Y)). These compounds are expected to function as more active catalysts for the production of poly- α -olefins with regular microstructures. A primary, long-term objective is the development of a truly "living" Ziegler-Natta catalyst system which would produce new types of polymers consisting of covalently linked homoblocks of different poly- α -olefins.

University of California, Irvine
Irvine, CA 92717

Department of Chemistry

259. Synthesis and Chemistry of Yttrium and Lanthanide Metal Complexes

Evans, W.J.

\$106,000

Comm. 714-856-5174

The special chemical, physical, and catalytic properties of compounds of yttrium and the lanthanide metals, a unique group of metals that are abundant in the U.S., are under investigation. The utility of compounds of these metals containing alkoxide and aryloxy ligands, which form strong metal oxygen bonds, as soluble, robust precursors to reactive organometallic species is being determined. The tert-butoxide ligand has been found to generate polymetallic complexes with these metals and

the multimetallic structure adds an extra means of controlling and manipulating reactivity. Synthetic studies have shown that a variety of mono-, bi-, and trimetallic complexes can be obtained by varying the alkoxide ligand. Good synthetic routes to these species have been established, as well as syntheses of extended lattice systems and larger molecular systems up to fourteen metals. This collection of alkoxide complexes provides the necessary synthetic base to develop the organometallic chemistry of this class of compounds. In addition, the synthetic studies have revealed new structural types of yttrium and lanthanide complexes which appear to have independently interesting chemistry. In general, these alkoxide complexes provide a range of new opportunities to better exploit the special chemistry available from these metals.

University of California, Santa Barbara
Santa Barbara, CA 93106

Department of Chemical and Nuclear Engineering

- 260. The Activation and Decomposition of Alkanes on Group VIII Transition Metal Surfaces: Dynamics, Kinetics, and Spectroscopy**
Weinberg, W.H. **\$86,500**
Comm. 805-893-8528

The project objective is to combine molecular beam techniques, mass spectrometric measurements in a bulb environment, and high-resolution electron energy loss spectroscopy (EELS) to provide as complete an understanding as possible concerning alkane activation and reactions on clean and chemically modified Group VIII transition metal surfaces. The hydrocarbon reactants studied are methane, ethane, propane, n-butane, i-butane, and cyclopropane; the surfaces employed, which display remarkably different reactivities, are Ir(110)-(1 x 2), Ir(111), Pt(110)-(1 x 2), and Ru(001). Selected measurements are planned to quantify the effects of adsorbed hydrogen and adsorbed oxygen on the surface reactions. The beam experiments clarify the dynamics of both direct and trapping-mediated alkane activation. The bulb experiments involve mechanistic studies with isotopically labeled molecules and the high-resolution EELS is employed to determine the rate of reaction and the pathway of subsequent dehydrogenation, hydrogenation, and decomposition reactions on the surface. Dynamic Monte Carlo simulations are planned to gain additional quantitative insight into the rates of a number of elementary surface reactions that occur during the alkane adsorption and activation.

Department of Chemistry

- 261. Studies Relevant to the Catalytic Activation of Carbon Monoxide**
Ford, P.C. **\$114,000**
Comm. 805-893-2443

This research is concerned with quantitative investigations of fundamental metal complex reactions which have

relevance to the homogeneous catalytic activation of carbon monoxide and other C₁ compounds. Work includes mechanistic studies of the formation and reactivities of nucleophile-carbonyl complexes, which are intermediates in a number of different catalytic processes, as well as continuous flow reactor studies of the water gas shift and related reactions as activated by solution phase or polymer supported metal carbonyl catalysts. Related investigations in progress are applications of fast reaction methodologies, principally laser flash photolysis with infrared or optical detection, to prepare and to study the reaction dynamics of reactive intermediates proposed as key species in the catalytic activation of CO, other C₁ compounds, hydrocarbons, and various small molecule substrates. The goals are to delineate the fundamental principles of such catalytic processes, thus to establish and extend molecular engineering guidelines for the design of new chemical systems for efficient use and applications of energy and chemical feedstock resources.

Colorado State University
Fort Collins, CO 80523

Department of Chemistry

- 262. Chemically Modified Electrodes and Related Solution Chemistry**
Elliott, C.M. **\$88,750**
Comm. 303-491-5204

The chemical and/or physical properties of electrode solution interfaces can be modified in useful ways by interposing thin polymer films at that interface. Such modifying films may contain bound electrochemically active catalyst molecules, or they may simply serve to alter the chemical environment in which the electron transfer event takes place. In studies under investigation, new schemes for incorporating electroactive systems into polymers that can be used to modify electrode surfaces are of interest. Additional research is aimed at developing and studying molecules that are of potential interest as catalysts which can subsequently be incorporated into electrode bound films. Specific areas of interest include (1) catalytic electrochemical oxidation of olefins employing polymer films of heteropolynuclear porphyrins; (2) electrocatalytic hydrogenation of unsaturated centers employing molybdenum-sulfur complexes; and (3) catalytic oxidation of water to form dioxygen. Other polymers under study form a new class of electronic conductors which may have applications to problems of catalysis by greatly increasing the effective surface area of electrodes. Several of these materials also have novel electrochromic and redox-adjustable ion exchange properties. The primary methods of investigation of these surfaces are electrochemical, including such techniques as chronoamperometry, cyclic voltammetry, and rotated disk voltammetry.

- 263. Diosmacycloalkanes as Models for the Formation of Hydrocarbons from Surface Methylene**
Norton, J.R. **\$166,951**
Comm. 303-491-5609 **(19 months)**

The stereochemistry of the formation of diosmacyclobutanes from olefins is under investigation. This reaction models the chemisorption of olefins onto metal surfaces,

and it is believed that both reactions retain stereochemistry about the double bond. Diosmacyclobutanes are also excellent vibrational models for olefins chemisorbed on metal surfaces, and it was found that the vibrational frequencies of an unsubstituted diosmacyclobutane agree very well with those of ethylene on Pt(III). The vibrational frequencies of an ethylidene-bridged diosmium complex are also being assigned, so that ethylidene species can be recognized on catalyst surfaces. Methods were also developed to use NMR in liquid crystal solvents to determine the structure of mononuclear and dinuclear ethylene complexes in solution. For the dinuclear ethylene complex, and unsubstituted diosmacyclobutane, the results agree well with those determined in the solid state by neutron diffraction.

**University of Colorado
Boulder, CO 80309**

Department of Chemistry and Biochemistry

264. Lewis Acid Modified Molybdenum Sulfide Complexes

DuBois, M.R.

\$74,685

Comm. 303-492-5039

The objective is to examine the effect of acids on the reactivity of molybdenum (Mo) sulfide sites in discrete dinuclear complexes. The project may provide a basis for evaluating the role of acids in the reactions of supported metal-sulfide catalysts. A recent focus of the project has been a kinetic and mechanistic study of the reactions of hydrogen with cationic complexes of the formula $[(C_5H_5Mo)_2(S_2CH_2)(\mu-S)(\mu-SR)]^+$, I. The reactions proceed to form a neutral hydrosulfido complex $(C_5H_5Mo)_2(S_2CH_2)(\mu-SH)(\mu-SR)$, II, and an equivalent of protons. Both the mechanism for the formation of H^+ in this reaction and the role of H^+ in promoting further reactions of the dinuclear complexes have been investigated. The rate of the reaction of hydrogen with cation I, where R = thienyl, showed a first order dependence on cation ($k_{obs} = 2.5 \times 10^{-4} \text{sec}^{-1}$), and a first order dependence on H_2 over a tenfold concentration range of each reagent. Reaction rates were independent of the nature of the amine used as proton acceptor. A significant deuterium isotope effect has been observed, and a preliminary determination of $k_H/k_D = 2.5$. The data are consistent with direct activation of H_2 by the cation to form a protonated derivative of II. Synthetic models for the proposed protonated intermediate have been characterized, and reaction pathways of these models are currently being studied.

**University of Connecticut
Storrs, CT 06269-3060**

Department of Chemistry

265. Structure Sensitivity of Cobalt/Iron Alloys and Clusters in Zeolites

Suib, S.L.

\$73,000

Comm. 203-486-2797

The goals of this research program are (1) to prepare bimetallic and alloy clusters of Co and Fe in zeolites; (2) to

study the sizes, shapes, compositions, structures, and physical properties of such clusters; and (3) to study the structure sensitivity of these metal clusters trapped in zeolites for reactions of cyclopropane and hydrogen. Several synthetic procedures are being carried out to prepare metal clusters in zeolites including microwave plasma decomposition of organometallic precursors, and thermal degradation of mixed metal precursors. The metal clusters are characterized with a variety of spectroscopic techniques in order to determine size, shape, electronic, structural, magnetic, and optical and surface properties. Such characterization methods include X-ray powder diffraction, ferromagnetic resonance, electron paramagnetic resonance, scanning and transmission electron microscopy, spin echo nuclear magnetic resonance, atomic absorption, and energy dispersive X-ray analysis. Characterization of zeolites containing, in particular, framework iron(III) ions as well as boron(III) ions is also being done. Luminescence, infrared, Mössbauer, and electron paramagnetic resonance studies are being done on these isomorphously substituted ions. Transient kinetic studies at atmospheric pressure show that H_2 can be encapsulated in sodalite cages of zeolites. Transient sorption and desorption studies with cyclopropane in various diluent gases suggest that intracrystalline diffusivities are influenced by the types and numbers of cations exchanged into the zeolite as well as metal clusters. Correlations among catalytic activity, selectivity, stability and size, shape, and properties of the metal clusters and zeolite structures are sought.

**University of Delaware
Newark, DE 19716**

Center for Catalytic Science and Technology

266. Chemistry of Oxygenates on Transition Metal Surfaces: Activation of C-H, C-C, and C-O Bonds

Barteau, M.A.

\$79,900

Comm. 302-451-8905

There can be little doubt that oxygen-containing hydrocarbons (oxygenates) will play an increasingly prominent role as components of motor fuels and, potentially, as raw materials for other petrochemical-based processes. The last decade has seen increasing use of oxygenates, including alcohol blends and methyl tertiary butyl ether (MTBE), as octane enhancers in gasoline. Current trends include the introduction of "environmental gasolines," reduction of some high octane hydrocarbons including butanes and aromatics, and legislative requirements for increased oxygen content as a means of improving air quality. This research focuses on the structural requirements of both surface and reactant for the activation of C-H, C-C, and C-O bonds of oxygen-containing molecules on transition metal surfaces of importance in oxygenate synthesis. Two principal questions are addressed: (1) Can the C-O bond of alcohols be activated by specific surface structures on metals such as rhodium and palladium and (2) What is the role of activation of β -CH bonds in determining the reaction sequence and selectivity of decarbonylation of higher oxygenates on these surfaces? These questions arise in attempting to explain a number of recent surprising observations from surface science experiments that

are directly relevant to mechanisms for oxygenate synthesis on transition metal catalysts. These include evidence for C–O scission in methanol on platinum and palladium surfaces, β -CH scission which precedes C–C scission in aldehyde decarbonylation on palladium but not on rhodium, and nonintersecting pathways for alcohol and aldehyde decomposition on rhodium. The results of these studies serve to illustrate the pathways, intermediates, and energetics of oxygenate reactions on group VIII metal surfaces and thus provide mechanistic insights into processes of practical importance, such as olefin hydroformylation and oxygenate synthesis from CO and H₂.

267. Characterization of Metal–Support Bonds in Supported Metal Catalysts

Gates, B.C.

\$91,700

Comm. 302-451-2347

The goal of this research is to characterize the structure and bonding of “molecular” metal complexes of tungsten, rhenium, osmium, iridium, and platinum, bonded to the surfaces of metal oxides (MgO, γ -Al₂O₃, and SiO₂). The surface complexes are synthesized by reaction of organometallic precursors such as metal carbonyls and allyls with the support surfaces, and characterized by EXAFS used in combination with temperature-programmed decomposition and infrared and NMR spectroscopies. These “molecular” precursors are treated to give highly dispersed metals and are characterized by the same techniques. The most thorough results have been obtained for rhenium carbonyls on alumina and magnesia. HRe(CO)₅ forms a surface complex formulated as Re(CO)₃(HOMg)_n(OMg)_{3-n}. The surface has been treated to vary the ratio of O to OH groups, and n has been varied from 0 to 3. The structures have distinctive infrared spectra, and the Re–O, Re–C, and Re–C–O bond distances determined by EXAFS spectroscopy characterize the electron donor properties of the surface ligands. Similar complexes are formed from H₃Re₃(CO)₁₂ on alumina, and when these are treated in hydrogen at 400°C, they form small trirhenium monolayer rafts. Re has two oxygen neighbors of the support, and the average Re–Re distance is 0.267 nm. Supported iridium carbonyls have been formed on MgO from Ir₄(CO)₁₂. The carbonyl ligands have been removed to give Ir₄ and Ir₆ clusters, and the metal–support interface has been characterized by EXAFS spectroscopy. For each, Ir–Mg and Ir–O distances have been determined and used to construct models of the metal–support interface, and infer the role of hydrogen at the metal–support interface.

Harvard University
Cambridge, MA 02138

Department of Chemistry

268. Mo-Catalyzed Heteroatom Removal Reactions: Effects of Promoters on Mechanism

Friend, C.M.

\$86,600

Comm. 617-495-4052

Molybdenum-induced sulfur and oxygen removal reactions have been investigated because of their importance in catalytic deoxygenation of fuels and desulfurization of fuel feedstocks. There has been emphasis on the effect of surface modification by sulfur and oxygen since they are

present during catalytic processing. Both sulfur and oxygen inhibit C–H bond breaking, leading to higher selectivity and slower kinetics for hydrocarbon production. Sulfur blocks the adsorption of reactive intermediates, resulting in lower yields of hydrocarbon. In contrast, oxygen does not inhibit adsorption, suggesting that it resides below the surface plane. Recent work suggests that the strength of the C–S and C–O bonds dictates the selectivity and kinetics for heteroatom removal by Mo. All experiments were performed under ultrahigh vacuum conditions on well-characterized single-crystal Mo using several surface spectroscopies. Current studies are concentrated on understanding the structure and HDS promotion effect of Co overlayers on Mo(110) with a p-(2 x 2) sulfur overlayer.

University of Illinois at Urbana-Champaign
Urbana, IL 61801

Department of Chemical Engineering

269. Selective Carbon Oxygen Bond Scission During Reactions of Oxygenates on Single Crystal Catalysts

Masel, R.I.

\$127,000

Comm. 217-333-6841

All of the previous studies of the decomposition of alcohols, aldehydes, and ketones on single crystals of group VIII metals have shown that the majority of the carbon–oxygen bonds stay intact during the decomposition process. However, recently it was discovered that the carbon–oxygen bond in methanol can be selectively broken if the surface structure of the platinum catalyst is appropriately tailored. The objective of this project is to determine whether this is general chemistry. The decomposition of a wide range of oxygenates on several carefully chosen faces of group VIII metals will be examined to see when C–O bond scission occurs. The surface chemistry of the resultant fragments will be studied and work directed toward the synthesis of higher hydrocarbons. The research will use a variety of surface spectroscopic techniques including temperature programmed desorption (TPD), X-ray-photoelectron spectroscopy (XPS), infrared (IR), electron energy loss spectroscopy (EELS), atmospheric pressure reactors, and molecular beams.

School of Chemical Sciences

270. Electron Transfer Activation of Coordinated Thiophene

Rauchfuss, T.B.

\$86,800

Comm. 217-333-7355

The project objective is to examine the reactivity of transition metal thiophene complexes. The work deals with metals known to be active catalysts for desulfurization and capitalizes on recent synthetic advances in the coordination chemistry of thiophene. A major area of interest is the effect of electron transfer on the structure, reactivity, and dynamics of coordinated thiophene. It is found that coordination can enhance the susceptibility of thiophene toward oxygen, hydroxide, and other metals. The mechanism and scope of these processes is being explored with attention to their relevance to novel desulfurization strategies.

Indiana University
Bloomington, IN 47405

Department of Chemistry

271. The Molecular Precursor Strategy for the Production of Superconducting OxidesCaulton, K.C. **\$109,600**
Comm. 812-855-4798

A molecular prerequisite for CVD or sol/gel conversion from molecular precursors $M_aM'_b(OR)_n$ to ceramic materials $M_aM'_bO_{n/2}$ is the synthesis of the binary metal alkoxides $M(OR)_m$ and also rational methods for linking these together at a controlled stoichiometry. Synthetic efforts have culminated in the synthesis and characterization of $Y_2(OSiPh_3)_6$ in the solid state and in solution. The anhydrous compound $Y(acac)_3$ is not monomeric, but gives deceptively simple ^{89}Y and 1H NMR spectra at 25°C. A new catalytic procedure for production of the barium precursor $[BaN(SiMe_3)_2]_n \cdot mTHF$ was developed and used to synthesize $[Ba(OSiPh_3)_2]_n \cdot nTHF$. Procedures were developed for coupling different metals together to produce soluble and volatile precursors. For example, $ClCuZr_2(OR)_9$ and also $Cu_4Zr_4O_3(OR)_{18}$ ($R = iPr$) were prepared and characterized. The latter displays certain structural features found in $YBa_2Cu_3O_7$, and magnetic studies show both ferromagnetic and antiferromagnetic interactions between the copper centers in this cluster. Also under investigation is the chemical basis for volatility enhancement by organofluoro groups in CVD precursors. The compound $Na_2Zr[OR']_6$ ($R' = CH(CF_3)_2$) is volatile, a consequence of its molecular character: the structure is described as $Na(\mu-OR')_2Zr(OR')_2(\mu-OR')_2Na$. Of special interest is the discovery that organofluoro groups bond to Na^+ via fluorine lone pairs. Such structural features explain why CVD with organofluoro precursors can leave inorganic fluoride in the resulting deposits.

272. Metal Alkoxides: Models for Metal OxidesChisholm, M.H. **\$124,000**
Comm. 812-855-6606

Polynuclear metal alkoxides of molybdenum and tungsten with the metal atoms in oxidation states +3, +4, and +6 contain M-M bonds that serve as electron reservoirs for the activation of small molecules and π -acids. The selection of a specific alkoxide ligand allows substrate selectivity. The organometallic chemistry of alkoxide clusters of Mo and W is being explored, with specific attention (1) to the cleavage of carbon monoxide to carbide and oxide, (2) to the cleavage of C=N, C=C, and N=N bonds, and (3) to the reactivity of the hydrido ligands in hydrido alkoxide clusters. Three classes of carbido tungsten clusters were structurally characterized: $W_4(OPr^i)_{12}(\mu_4-C)(\mu_2-O)$, $W_4(OCH_2Bu^t)_{12}(\mu_4-C)(\mu_2O)$ and $W_4(OCH_2R)_{14}(\mu_4-C)$ where $R = Pr$ and cyclo-pentyl, -butyl, and -hexyl. All are derived from the low temperature cleavage of CO. Competitive with the cleavage of carbon monoxide is additional CO uptake to yield compounds such as $W_4(\mu_4-CO)(CO)_2(OCH_2R)_{12}$. The hydrido ligands in $W_4(H)_2(OPr^i)_{14}$ and $W_2(H)(0-cy-pentyl)_7(L)$, where $L = HNMe_2$ or PMe_3 , have been found to react with a variety of unsaturated hydrocarbons including olefins, alkynes, dienes, nitriles and aldehydes and ketones. A number of products have been isolated and fully characterized including novel ethylene-ethyl and allene adducts.

The detailed mechanistic aspects of these reactions are under study by use of kinetic measurements and atom labeling studies.

273. A Model Approach to Vanadium Involvement in Crude Oil RefiningChristou, G. **\$98,600**
Comm. 812-855-2399

This research is directed toward (1) identifying the types of nonporphyrin vanadium (VO^{2+}) impurities in crude oils and (2) determining the mechanistic pathways by which they are reduced, de-ligated, and sulfided under hydrometallization (HDM) and hydrodesulfurization (HDS) conditions. As part of this identification process, investigation is continuing into the reactivity characteristics of VO^{2+} complexes under reducing conditions, with S/S, S/N, O/S and O/N ligands, to better model the true oil impurities. In all cases, vanadium(III) complexes of various nuclearities are the products, with either partial or complete loss of the VO^{2+} oxygen. A systematic effort is in progress to assemble and study V_x/S_y aggregates, to model vanadium sulfide polymer formation, and mixed-metal V/Mo/S aggregates, to model the initial deposition and poisoning of the Mo HDS catalyst. A variety of products, including $[V_3S(S_2)_3(bpy)_3](PF_6)$ have been obtained.

274. Free-Radical and Concerted Reactions in Coal LiquefactionGajewski, J.J. **\$100,000**
Comm. 812-855-1192

Efforts are continuing to understand the high-temperature cleavage reaction of alkyl-aromatic coal liquefaction model compounds. In addition, the pyrolysis of 5-methylenespiro[3,5]nonane was studied. This material undergoes a retro 2 + 2 cleavage and a 1,3-shift to $\Delta^{1,2}$ -octalin in a 1:2 ratio, respectively. Comparison of the activation parameters suggests that the rearrangement in unbiased systems results from an unfavorable entropy of activation and the secondary deuterium kinetic isotope effect at the exomethylene carbon is normal at 1.086 for two deuteriums, all of which is consistent with a concerted reaction. The 5-methylenespiro[3,5]nona-1-ene was prepared, and its thermal rearrangement to $\Delta^{1-2,3}$ -hexalin was examined. Also formed is a triene resulting from cyclobutene ring opening. Kinetic modeling suggests that the triene reverts to either starting spirodiene or gives the hexalin directly. It is likely that both possible trienes are formed, but the *cis* material cyclizes immediately to hexalin, and the *trans* isomer is the visible component. Work continues on developing a force-field appropriate to organometallic systems. The model assumes that all metal ligand bond distances are a function of the ligand and the covalent radius of the metal, and it ignores bond angle and torsion potentials. Simplex optimization has allowed refinement of the original set to more accurately reproduce a vast array of organometallic structures provided that the metal is coordinately saturated and is not early in the periodic table.

University of Iowa
Iowa City, IA 52242

Department of Chemistry

- 275. Synthesis and Chemistry of Cationic d^0 Metal Alkyl Complexes**
Jordan, R.F. **\$87,755**
Comm. 319-335-2212

The objective of this research is to design and synthesize new types of electrophilic metal alkyl complexes for use in fundamental studies of olefin polymerization and C-H activation chemistry. Earlier studies of cationic $Cp_2Zr(R)(L)^+$ complexes ($L =$ labile ligand) support recent proposals that $Cp_2M(R)^+$ ions are the active species in Cp_2MX_2 -based olefin polymerization catalysts. Recent studies of these systems have focused on solution structures and dynamics. X-ray diffraction and spectroscopic studies establish that the alkyl ligands of the $Cp_2Zr(R)(L)^+$ ($L = PMe_3, CH_3CN$) complexes are distorted by β -agostic interactions. The alkyl ligand of $(C_5H_4Me)_2Zr(CH_2CH_2SiMe_3)(L)^+$ ($L = THF, PMe_3, CH_3CN$) is distorted by a strong Zr- β -C interaction. These studies suggest that the alkyl ligands of the $Cp_2Zr(R)^+$ and $Cp_2Zr(R)(olefin)^+$ ions in olefin polymerization reactions also adopt distorted (ground state) structures. Efforts are under way to probe how/whether these structural features influence insertion reactivity and/or stereochemistry. Studies of new group 4 metal complexes which incorporate ancillary ligand systems other than Cp_2M have been initiated to test the generality of the conclusions of the $Cp_2M(R)^+$ studies. To probe the influence of charge on reactivity, neutral $d^0 (C_2B_9H_{11})(Cp^*)M(R)$ ($M = Zr, Hf$) complexes which incorporate the dinegative, 6-electron donor ligand $C_2B_9H_{11}^{2-}$ (dicarbollide) in place of the uninegative Cp^- were prepared. This formal substitution reduces the metal charge by one unit but does not greatly change the metal frontier orbital properties. The reactivity of these new systems is comparable to that of their cationic $Cp_2Zr(R)^+$ analogues: $(C_2B_9H_{11})(Cp^*)MR$ complexes polymerize ethylene, oligomerize propene, insert acetylenes, and undergo internal C-H activation/ CH_4 elimination to yield μ - CH_2 complexes $[(C_2B_9H_{11})(Cp^*)M]_2(\mu-CH_2)$. These results suggest that metal unsaturation may be more important than charge for high insertion and σ -bond metathesis reactivity.

University of Kentucky
Lexington, KY 40506-0055

Department of Chemistry

- 276. Metallacumulenes and Carbide Complexes**
Selegue, J.P. **\$121,310**
Comm. 606-257-3484

The synthesis, characterization, and reactivity of metallacumulenes (cumulated transition metal carbene complexes) and low-coordinate carbide complexes ($C_1, C_2,$ or C_3 fragments bonded to four or fewer metal centers) are under study. These compounds serve as models for reactive, carbon-rich intermediates which are formed on the surfaces of heterogeneous transition-metal catalysts during reactions of carbon monoxide and 1-alkynes

(terminal acetylenes). Whereas 1-alkynes typically react with d^6 iron(II) or ruthenium(II) moieties $[M(PR_3)_2(Cp)]^+$ ($Cp = \eta^5$ -cyclopentadienyl) to give vinylidene complexes $[M(C=CHR')(PR_3)_2(Cp)]^+$, for small phosphine ancillary ligands kinetic alkyne isomers $[M(\eta^2-HC\equiv CR')(PR_3)_2(Cp)]^+$ can be isolated. These rearrange to the thermodynamic vinylidene isomers at temperatures from room temperature to $80^\circ C$. Both forms of $[Ru(C_2H_2)(PMe_2Ph)_2(Cp)][BF_4]$ have been structurally characterized. In general, rearrangements are faster for iron than ruthenium, and for larger ancillary ligands. As an approach to unknown bis(vinylidene) complexes, the deprotonation of $[W(CO)(C\equiv CMeCMe_3)(\eta^2-HC\equiv CMe_3)(Cp^*)][BF_4]$ ($Cp^* = \eta^5$ -pentamethylcyclopentadienyl) was carried out under carbon monoxide. The structurally characterized enynyl complex $[W(CO)_2(\eta^3-Me_3CC\equiv C-CMeCMe_3)(Cp^*)]$ resulted from facile intramolecular alkynyl-vinylidene coupling. Preparations and reactions of new diphenylallenylidene complexes $[M(C\equiv C=CPh)_2L_2(Cp)]^+$ are under study. When $[Ru(C\equiv CMe)(CO)_2(Cp)]$ reacts with stoichiometric or catalytic amounts of either $[W(CEt)(OCMe_3)_3]$ or $[W_2(OCMe_3)_6]$ in isooctane, the ethynediyl complex $[\{Ru(CO)_2(Cp)\}_2(\mu-C\equiv C)]$ precipitates in good yield. The $C\equiv C$ bridge is reactive, combining with $[Fe_2(CO)_9]$ to give crystallographically characterized $[Ru_2Fe_2(\mu_4-C_2)(CO)_9(Cp)_2]$. Mixed-metal ethynediyls $[(Cp)L_2M(\mu-C\equiv C)W(PhC\equiv CPh)(CO)(Cp)]$ ($M = Fe, Ru; L = PMe_3, P(OMe)_3$, and so forth) result from the deprotonation of cationic ethynyl-bridged precursors.

Lehigh University
Bethlehem, PA 18015

Department of Chemistry

- 277. Infrared Study of Carbon Deposits on Bimetallic Catalysts**
Eischens, R.P. **\$85,000**
Comm. 215-758-3600

The objective of this research program is to determine how the addition of a second metal (such as rhenium, iridium, or tin) to a platinum/alumina reforming catalyst affects the nature of carbon deposition on the catalyst. Carbon deposition is followed by *in situ* measurement of weight increases and changes in the infrared spectra. In each case the added component (rhenium, iridium, or tin) lowers the formation of a carboxylate species, which is detected by infrared bands at 1585 and 1460 cm^{-1} . Current emphasis is on the study of the mechanism of carboxylate formation. The higher frequency, i.e., the more basic, surface hydroxyls of alumina provide the oxygen for carboxylate formation. Carboxylates are not formed on amorphous or crystalline silica alumina. Thus, mechanisms which postulate Al-O-Al linkages appear to be supported.

- 278. Mechanisms and Controlling Characteristics of the Catalytic Oxidation of Methane**
Klier, K.; Simmons, G.W.; Her- **\$115,000**
man, R.G.; Miller, A.C.
Comm. 215-758-3577

Surfaces that are active for the activation of methane on palladium(100), (311), and (679) surfaces, including O/ CH_2Cl_2 /Pd(100) overlayers, were studied by AES/LEED/

TDS and HREELS. With oxygen adsorbed on the Pd(100) surface, the previously observed disproportionation of the $(2 \times 2)\text{-O}$ structure into a mixture of a dense phase, $(\sqrt{5} \times \sqrt{5})\text{R}27^\circ\text{-O}$, and a rare phase, (2×2) , is accounted for by a reconstruction-relaxation process of the Pd(100) surface that arises as a response to a critical coverage at a critical temperature. The O/Pd(100) study suggests that the rare adsorbed oxygen phase with a surface coverage = 0.25 monolayer (ML), achievable at 650 K and low partial pressure of oxygen, is the most reactive state for oxidation reactions. Dichloromethane, used to control oxidation of methane to formaldehyde over supported Pd catalysts, is adsorbed dissociatively on the Pd(100) surface. This adsorption proceeded with a near-unity initial sticking coefficient and reached saturation with Cl coverage of 0.22 ML. The surface structures formed, as well as their interactions with O, have been modeled and fitted to the CH_2Cl_2 adsorption data, and the best features are obtained with surface Cl-C-Cl ensembles, having 90° Cl-C-Cl angles, that exclude nearest-neighbor adsorption and Cl-Cl next-nearest-neighbor adsorption. A Monte Carlo simulation of the oxidation of surface carbon by surface oxygen atoms semiquantitatively explains selective oxidation to CO_2 on Cl-free Pd and to CO on Pd covered by some 20% Cl atoms in terms of a restricted supply of oxygen partially Cl-covered surfaces that can be regarded as ensemble control of the oxidation reaction. A high-pressure cell in the ultrahigh vacuum (UHV) apparatus was used to show the Pd(679) surface was more active for activation of oxygen and methane than the Pd(100) surface.

**Louisiana State University
Baton Rouge, LA 70803-0301**

Department of Chemistry

**279. Studies of Metal-Ammonia Interactions
with Aromatic Substrates**

Rabideau, P.W. **\$80,000**
Comm. 504-388-8859

Dissolving metal reduction reactions are important to coal chemistry, since these methods, when applied to coal, promote solubilization and depolymerization. Solubilization is important to liquefaction, as well as to the characterization of coal structure since the soluble fractions can be analyzed spectroscopically. This research program has focused on a better understanding of the reduction pathway using polynuclear aromatics (PAS) as model compounds. Included are studies of the reaction mechanisms, and attempts to understand the structural and geometric features of the anionic intermediates. For example, recent work involving theoretical calculations and NMR spectroscopy elucidates the position of the metal counterions in the dihydropleiadene dianion. It was found that ion triplets represent the preferred arrangement. The position of lithium metals in dilithiodiindenide (with indene units connected in 1,1'- and 1,2'-arrangements) is also being investigated. Barriers to rotation around the connecting bond were determined, and the dependence on solvent allows insight into the nature of ion pairing in this system. Projects using silicon to control reduction continue, and recently several hydrofluorenes were isolated

by this method. Some of these compounds have been implicated in hydrogenation reactions, but never isolated because of complex reaction mixtures in the latter process.

**University of Louisville
Louisville, KY 40292**

Department of Chemistry

280. Metalloxy-carboxylate Chemistry

Gibson, D.H. **\$87,000**
Comm. 502-588-5977

The chemistry of metalloxy-carboxylates (M-COOR ; $\text{R} = \text{H}$, alkyl, main or transition metal) is under investigation; the compounds are models for catalytic intermediates in the water gas shift reaction or in CO_2 fixation processes. Successful work on the synthesis and characterization of anhydrous metalloxy-carboxylate anions, $\text{CpFe(CO)(PPh}_3\text{)CO}_2\text{M}$ ($\text{M} = \text{Li, K}$) and $\text{Cp}^*\text{Fe(CO)(PPh}_3\text{)CO}_2\text{K}$ has been followed by an extensive study of their reactions (and those of their hydrated analogs) with protonic acids and methylating agents. These studies have revealed a pattern of competitive electrophilic cleavages of the carboxylate C-O and O-M bonds which are dependent upon the oxophilicity of the alkali metal and the electron donor capabilities of the other ligands bound to the iron atom. The more highly oxophilic lithium ion promotes C-O bond cleavage; the Cp^* ligand also promotes C-O bond cleavage when compared to Cp, apparently by enhancing the carbenoid character of the iron-carboxylate carbon bond in the anion. Work has been initiated to synthesize and characterize bimetallic compounds derived from the metalloxy-carboxylate anions which have carboxylate bridging ligands between iron and a main group or late transition metal. CO_2 -bridged iron-tin complexes were characterized first. Recently, several compounds were prepared with another late transition metal such as iron or rhenium as the second metal center; characterization of these compounds is in progress.

**Massachusetts Institute of Technology
Cambridge, MA 02139**

Department of Chemistry

**281. High-Pressure Heterogeneous Catalysis in
a Low-Pressure, Ultrahigh Vacuum Environment**

Ceyer, S.T. **\$96,000**
Comm. 617-253-4537

The major thrust of this proposed research is to carry out for the first time a heterogeneous catalytic reaction that normally is observed only at high pressures (≥ 1 atm) of reactant gas at low pressures ($\leq 10^{-4}$ torr) in an ultrahigh vacuum environment on a Ni(111) crystal surface. This is possible using a scheme that couples molecular beam techniques with high-resolution electron energy loss spectroscopy (HREELS). Two molecular beams provide a means to activate each of the two reactants, and the HREELS is a sensitive and chemically specific detector of the reaction progress. These studies will verify the principles behind the lack of reactivity at low pressures. The

ability to carry out a "high-pressure" reaction, such as the steam reforming of CH_4 , in a UHV environment enables the use of surface-sensitive electron spectroscopies such as HREELS to identify unambiguously the reaction intermediates, thereby testing the mechanisms proposed from high-pressure kinetics measurements. Work has begun on the design of the apparatus.

282. Controlled Synthesis of Polyenes by Catalytic Methods

Schrock, R.R.

\$123,700

Comm. 617-253-1596

This project concerns the synthesis of organic conductors and related nonlinear optical materials, specifically polyenes at this stage, using well-defined transition metal complexes. It was shown that 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (TCDT-F6) can be ring-opened in a controlled manner by $\text{M}(\text{CH-t-Bu})(\text{NAr})(\text{O-t-Bu})_2$ ($\text{M} = \text{Mo}$ or W ; $\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-i-Pr}_2$) to give living oligomers from which the metal can be removed in a Wittig-like reaction with pivaldehyde or 4,4-dimethyl-*trans*-2-pentalen. Heating the oligomer yields a distribution of *t*-butyl-capped polyenes, $(\text{t-Bu})(\text{CH}=\text{CH})_x(\text{t-Bu})$, where x is odd if pivaldehyde is used in the cleavage reaction, or even if 4,4-dimethyl-*trans*-2-pentalen is used. The retro Diels-Alder reaction was carried out on the living TCDT-F6 oligomers to give "living polyenes," $\text{W}[(\text{CHCH})_x(\text{CH-t-Bu})(\text{NAr})(\text{O-t-Bu})_2]$, that are stable toward "back-biting" to give benzene, and thermally stable up to $x = 10$ to 12. These are now being used as reagents in Wittig-like reactions with unsaturated dialdehydes such as $\text{OHCCH}=\text{CHCH}=\text{CHCHO}$ and $\text{OHCCH}=\text{CHCH}=\text{CHCH}=\text{CHCHO}$ in order to prepare long polyenes. Living polyenes can also be prepared by the direct controlled polymerization of acetylene itself. The possibility of polymerizing substituted acetylenes in a controlled fashion is under investigation. The goals include a complete understanding of why and how polyenes of intermediate conjugation length (15 to 20 double bonds) crosslink, and an understanding of the relevance of that behavior to the nature of classical polyacetylene. Physical measurements on materials that are being made include (through collaborations) third-order nonlinear optical behavior, spectroscopy of radical cations in low-temperature matrices, and conductivity via microelectrode techniques.

University of Massachusetts at Amherst
Amherst, MA 01003

Department of Chemical Engineering

283. Kinetics and Dynamics of Oxidation Reactions Involving an Adsorbed CO Species

Harold, M.P.

\$69,100

Comm. 413-545-6143

This research involves integrated experiments and modeling of oxidation reactions involving CO as a key player, be it a reactant, adsorbed intermediate, and/or partial oxidation product, in the catalytic sequence and chemistry. The reaction systems studied include bulk and supported Pt-catalyzed formaldehyde and methanol oxidation and copper oxide-catalyzed CO oxidation by O_2 and NO. The

overall project objective is to formulate kinetic models that are built upon rational mechanistic sequences, and that can predict the measured basic kinetic trends, the location and shape of the operating condition region(s) for which the rate is multivalued or periodic, and the trends in the adsorbed state composition. The research consists of three components. In part (1) apparent reaction orders and activation energies and regions of rate multiplicity or oscillations are measured. The experiment accommodates either metal wire or supported catalysts, and is designed for a wide range of total pressures, catalyst temperatures, and feed compositions. In part (2) Fourier transform infrared emission spectroscopy (FTIRES) is developed as a new spectroscopic tool to monitor characteristic adsorbate, adsorbate-substrate, and substrate vibrational modes during reaction. For example, during CO oxidation by NO on copper oxide, FTIRES is used to monitor adsorbed CO and the two oxidation states of copper oxide. These measurements help to elucidate the link between the metal oxidation state and catalytic activity and selectivity, and possible nonlinear spatio-temporal phenomena. Part (3) integrates the kinetic and surface measurements in (1) and (2), established kinetics of elementary steps (e.g., from UHV studies), and nonlinear analysis tools to formulate predictive kinetic models. For multivalued rate data, singularity theory is used to determine if a kinetic model can predict observed multiplicity features. Regression schemes are used to estimate kinetic parameters based on a fit of the operating condition region within which multiplicity is observed.

University of Michigan
Ann Arbor, MI 48109-1055

Department of Chemistry

284. Hydrogen Induced C-C, C-N, and C-S Bond Activation on Pt and Ni Surfaces

Gland, J.L.

\$162,000

Comm. 313-764-7354

(18 months)

Hydrogenolysis of well-characterized adsorbed organic monolayers by coadsorbed atomic hydrogen on single crystal surfaces of Ni and Pt is the primary focus of this research. The structure and coordination modes of adsorbed reactants will be varied in a systematic way in an effort to characterize hydrogen addition selectivity and the kinetics of elementary hydrogen addition processes on well-characterized metal single-crystal surfaces. Nickel and platinum surfaces have been chosen to represent surfaces with high and low hydrogenolysis activity. The addition of adsorbed atomic hydrogen to C-C, C-N, and C-S bonds in adsorbed species of the type $-\text{CH}_2\text{R}$, $-\text{NH}_2\text{R}$ and $-\text{SR}$ will be characterized where R represents attached methyl, cyclohexyl, and phenyl groups. *Ex situ* interrupted reaction studies will be used to characterize monolayer hydrogen addition reactions for hydrogen pressures up to 10^{-4} torr by focusing on the adsorbed species remaining on the surface after reaction. *In situ* kinetic experiments will be performed for promising hydrogen addition reactions using fluorescence yield near edge spectroscopy (FYNES) to characterize the structure and reactivity of adsorbed carbon containing monolayers in pressures up to 10 torr of hydrogen. Basic understanding of the primary factors that control hydrogen addition selectivity and reactivity on

metal surfaces will be increased by focusing on the issue of hydrogen induced bond activation on metal surfaces.

University of Minnesota Minneapolis, MN 55455

Department of Chemical Engineering and Materials Science

285. *Homogeneous-Heterogeneous Combustion: Chemical and Thermal Coupling*

Schmidt, L.D.

\$85,500

Comm. 612-625-9391

The roles of homogeneous and heterogeneous reactions in combustion processes are being studied experimentally and theoretically by examining the concentration and temperature profiles near reacting surfaces and by calculating these profiles for known kinetics. Laser-induced fluorescence methods are being developed to measure the concentrations of free radical intermediates near reacting surfaces for the $\text{NH}_3 + \text{O}_2 \rightarrow \text{NO}$, $\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}$, and $\text{CH}_4 + \text{NH}_3 + \text{O}_2 \rightarrow \text{HCN}$ reactions on polycrystalline platinum and rhodium as functions of surface temperatures and reactant composition, pressure, and temperature. The concentrations and internal temperatures of OH, NH, CN, and other radical intermediates with and without homogeneous reaction will be measured directly. Concentration and temperature profiles are also being calculated for various reaction processes and flow conditions. Of particular interest is the bifurcation behavior (occurrence of multiple steady states and oscillations) for various models of homogeneous-heterogeneous processes. Reaction rate expressions for individual surface and homogeneous reactions are used to simulate the experimentally observed behavior. The objective of this research is to understand the contributions of each type of reaction in practical situations in catalytic reactors and combustors in order to determine their implications in reactor selectivity and pollution abatement. Rates and selectivities in $\text{CH}_4 + \text{NH}_3 + \text{O}_2$ reactions over Pt to produce HCN have been compared over ceramic and metal monoliths. An essential feature in determining HCN yield appears to be the hydrolysis reaction which occurs homogeneously.

University of Missouri at Columbia Columbia, MO 65211

Department of Chemistry

286. *Late Transition Metal μ -Oxo and μ -Imido Complexes*

Sharp, P.R.

\$106,062

Comm. 314-882-7715

The synthesis and reactions of oxo, imido, dioxygen, and nitrosoarene complexes of the late transition metals are being studied. Interest in these complexes is primarily as models for species on late transition metal surfaces. The goal is to develop the chemistry of these model complexes as an aid to understanding the many important catalytic reactions that occur on late transition metal surfaces. Initial efforts at developing synthetic procedures for the oxo

and imido complexes have been successful and have produced complexes that do mimic many of the properties of the analogous surface species. These properties include high basicity and oxo and nitrene transfer activity. The exploration of the versatility of these synthetic procedures and the reaction chemistry of the complexes is continuing. Unique reactivity leading to C-C bond formation associated with the high basicity of arene imido complexes has been found and may have applications in synthetic organic chemistry. Also being explored is the possibility of a dioxygen-to-dioxo pathway to the oxo complexes. This would amount to molecular oxygen activation and would mimic another property of the metal surfaces. An important part of this effort is the synthesis, using already established methods, of oxo (and imido) complexes that can be targeted for formation from dioxygen.

University of Nevada Reno, NV 89557-0020

Department of Chemistry

287. *High-Temperature Chemistry of Aromatic Hydrocarbons*

Scott, L.T.

\$93,670

Comm. 702-784-6683

This work focuses on the fundamental molecular processes involved in the rearrangements and interconversions of polycyclic aromatic hydrocarbons (PAHs) under conditions of thermal activation. PAH ring systems figure prominently in the molecular architecture of coal, but prior to the initiation of this project, little was known about the chemical transformations that PAHs undergo at the high temperatures employed in the uncatalyzed gasification and liquefaction of coal. The startling discovery of benzenoid ring contraction reactions has opened the door to a wide range of mechanistic studies, and evidence for the reversible generation of carbene intermediates from aromatic rings continues to accumulate. The 1,2-switch of carbon atoms first observed in ^{13}C -labeled naphthalene has been uncovered also in other aromatic hydrocarbons by ^{13}C -labeling, and rings in which benzannulation reduces the aromaticity have been found to rearrange faster than those bearing a closer resemblance to benzene. A double-labeling experiment with *trans*-stilbene has revealed the corresponding 1,2-switch of carbon atoms in a nonaromatic alkene. The long-range objectives of this research are to uncover all the principal reaction channels available to PAHs at high temperatures and to establish the factors that determine which channels will be followed in varying circumstances.

University of New Mexico
Albuquerque, NM 87131

Department of Chemistry

**288. Anchoring Strategies for Bimetallic
Species in Zeolites**

Bein, T.

\$210,443

Comm. 505-277-4935

(23 months)

This research program is aimed at understanding new immobilization concepts for organometallic fragments in the crystalline pore structure of zeolites. The approach taken is to introduce heterobinuclear organometallic compounds containing appropriate ligands as candidates for linking a catalytic function to zeolite frameworks. The bimetallic complexes $\text{Cl}_2(\text{THF})\text{GeM}(\text{CO})_5$ ($\text{M} = \text{Mo}, \text{W}$), and $\text{X}_3\text{SnMn}(\text{CO})_5$ ($\text{X} = \text{Me}, \text{Cl}$), have been reacted with different acidic, large pore zeolites. Extended X-Ray Absorption Fine Structure (EXAFS) studies reveal that the precursors are attached to the zeolite oxygen framework via the Ge or Sn moiety by loss of chloride or methyl ligands, while the carbonyl moiety remains largely intact at moderate temperatures. At higher temperatures, cleavage of the metal-metal bonds is observed. A comprehensive combination of analytical techniques is used to probe local structural changes at the molecular level. These techniques include EXAFS spectroscopy utilizing synchrotron radiation, *in situ* FT-IR coupled to thermodesorption, and Raman and reflectance UV-Vis spectroscopies. Diagnostic catalytic studies of hydrocarbon conversions will address issues such as the location of catalytically active sites, stability against migration, and shape selectivity introduced by the molecular sieve pore structure. The long-term goal is also to prepare intrazeolite bimetallic clusters through controlled decomposition of zeolite-anchored heterobimetallic compounds.

University of North Carolina at
Chapel Hill
Chapel Hill, NC 27599-3290

Department of Chemistry

**289. Reductive Coupling of Carbon Monoxide
to C_2 Products**

Templeton, J.L.

\$171,000

Comm. 919-966-4575

(18.5 months)

Coupling reactions involving carbon monoxide and carbyne ligands are being explored. A simple CH carbyne complex has been prepared by two routes. Addition of methyl iodide to $\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{H})\text{PR}_3$ allows isolation of small amounts of $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{CH}$. Treatment of a silylcarbyne precursor with wet R_4NF salts provides a route to larger quantities of this parent carbyne product. The monomer slowly dimerizes to form an unusual nonclassical vinylidene bridged dimer. A rare aryloxycarbyne complex has been prepared by nucleophilic attack on a phosphonium carbyne unit with phenoxide reagent. Electrophilic attack at the oxygen of a terminal carbonyl ligand to generate related alkoxycarbyne ligands is a long-term goal. In modeling this chemistry it was found that electrophilic addition to isonitrile ligands can generate

aminocarbyne products or η^2 -iminoacyl complexes. The η^2 -iminoacyl complexes are sufficiently acidic at the C_{sub β } position that deprotonation/alkylation sequences succeed in elaborating the η^2 -iminoacyl substituent.

Northwestern University
Evanston, IL 60208-3120

Department of Chemical Engineering

290. Solid-State, Surface, and Catalytic Studies of Oxides

Kung, H.H.

\$120,000

Comm. 708-491-7492

The selective conversion of low-priced saturated hydrocarbons to unsaturated hydrocarbons, aromatics, alcohols, aldehydes, or acids that are of much higher values can be of great technological importance. The emphasis of this project is to elucidate the properties of oxidic catalysts that could achieve these conversions efficiently by selective oxidation. For practical purposes, the ability to produce only one desired product among many possibilities, some of which are extremely thermodynamically favorable, is important. The relationship between surface atomic structure and bulk structure of an oxide with the catalytic properties is being studied using the oxidation of light alkanes as a test reaction. Earlier work showed that orthovanadates of magnesium, samarium, and neodymium were more selective catalysts than that of europium. It was proposed that the redox property of M in the M-O-V bonds in these oxides was a significant factor that affected selectivity. This concept was further tested by studying the oxidation of butane over orthovanadates of Cu, Al, Zn, Fe, Cr, and Bi. By combining these and the earlier data, it was found that orthovanadates of more reducible cations were less selective in oxidative dehydrogenation. Furthermore, the participation of lattice oxygen of some of these orthovanadates in the reaction was demonstrated when it was shown that the activity and selectivity of the catalyst were the same in the presence and absence of gaseous oxygen, until the catalyst was severely reduced. Separately, it was found that unlike Mg orthovanadate, Mg pyrovanadate was quite selective for propane although nonselective for butane. Thus, there is a specific interaction between a molecule and the oxide catalyst that depends on the structure of the molecule and the oxide surface.

Department of Chemistry

**291. Supported Organometallic Complexes:
Surface Chemistry, Spectroscopy, and
Catalysis**

Marks, T.J.

\$97,548

Comm. 708-491-5658

The project objective is to understand at a fundamental level the dramatic and technologically important changes in catalytic activity that occur when metal hydrocarbyl molecules are adsorbed on metal oxide and metal halide surfaces. The approaches involve integrated surface chemical (product analysis, isotopic labeling), catalytic (chemoselectivity, kinetics), and spectroscopic (CPMAS NMR, FT-IR) studies of selected actinide, lanthanide, and

group 4 organometallic molecules adsorbed on high surface area Al_2O_3 , SiO_2 , MgCl_2 , and other inorganic supports. A parallel solution chemistry effort focuses on the synthesis and structural characterization of complexes that spectroscopically and chemically reproduce the surface environment and verify ideas about the chemistry. A detailed kinetic/mechanistic study has been completed on hydrogenation of a variety of olefins by $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{Al}_2\text{O}_3$ and $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{MgCl}_2$, where $\text{Cp}' = (\text{CH}_3)_5\text{C}_5$. There are striking mechanistic similarities to f-element reaction patterns in solution. NMR studies reveal that unsaturated cationic complexes of the type $\text{Cp}'_2\text{ThCH}_3^+$ and $\text{Cp}_2\text{ZrCH}_3^+$ ($\text{Cp} = \text{C}_5\text{H}_5$) are formed in large quantities on Al_2O_3 and MgCl_2 surfaces. Cationic organothorium species have also been identified on other Lewis acid supports, and dosing with various reagents affords a detailed, *in situ* picture of the surface reaction chemistry. Good agreement is found between the percentage of active sites deduced by catalytic poisoning and NMR studies. Successful synthetic routes to such highly reactive f-element and group 4 cations have now been developed in solution and several crystal structures completed.

292. Chemical Interactions in Multimetal-Zeolite Catalysts

Sachtler, W.M.H.

\$104,000

Comm. 708-491-5263

Cobalt, nickel, copper, and gallium ions can be exchanged into zeolites, but their reduction requires severe conditions and often remains incomplete. The reducibility of cobalt, nickel, and copper can be dramatically enhanced by (1) washing at high pH and/or (2) adding platinum or palladium ions and placing them into specific zeolite cavities. The mechanisms leading to the formation of bimetallic particles in zeolite cages have been identified. At elevated temperature metal reduction is partially reversible: Cu in PtCu or PdCu particles and Ni in PdNi are selectively oxidized by zeolite protons to Cu^{2+} or Ni^{2+} ions which escape to smaller zeolite cavities. For PdCu and PdNi the resulting Pd particles are identified by their ability to form a hydride. Subsequent reduction in H_2 identifies the TPR peak characteristic of the reduction of Cu^{2+} or Ni^{2+} ions in contact with Pd particles. Zeolite Y encaged PdNi particles are found to be much more active methanation catalysts than either of the pure elements in Y. Ga/H-ZSM5 is active in converting alkanes (e.g., C_3) into aromatics; it was confirmed that catalyst reduction leads to enhanced activity. TPR reveals that reduction of Ga in H-ZSM5 starts at a significantly lower temperature than reduction of SiO_2 supported Ga_2O_3 . The presence of Pt enhances the reduction of Ga^{3+} to Ga^{1+} , but no PtGa alloy appears to be formed.

293. Organometallic Surface Chemistry

Shriver, D.F.

\$102,000

Comm. 708-491-5655

This research is focused on the reactions of ligands attached to clusters and the relation of these reactions to reactions on metal surfaces. Because of their importance in surface chemistry and catalysis most of this research concerns the oxo, carbido, and hydrido ligands and their derivatives. Extensive chemistry is observed for the carbido ligand, which for example can be converted to the CCO ligand and from there to acetylide and acetylene ligands. The chemistry of cluster bound oxygen is somewhat

more limited but a recently found example demonstrates that the oxo ligand can be an effective nucleophile. Also under study is the activation of H_2 by clusters. Facile reactions of H_2 with cluster-bound ligands have been found.

University of Oklahoma Norman, OK 73019

Department of Chemistry and Biochemistry

294. Transition Metal-Mediated Thermal and Photochemical Carbon Dioxide Activation

Nicholas, K.M.

\$100,819

Comm. 402-325-4811

The focus of this project is on the thermal (dark) and photochemical reactivity of carbon dioxide coordinated to transition metal centers. Efforts are centered on defining the fundamental reactivity patterns of selected, structurally characterized η^2 -mononuclear CO_2 complexes: (1) under thermal (dark) conditions toward external reagents including electrophiles, nucleophiles, and radical reagents and (2) under photolytic conditions. Following discovery of the remarkably facile reactions of $\text{Cp}_2\text{Mo}(\eta^2\text{-CO}_2)$ with various electrophilic reagents (E-Nu) which afford $\{\text{Cp}_2\text{Mo}(\text{CO})\text{Nu}\} + \text{Nu}^-$ and E-O-E, it was found that **1** reacts with acidic transition metal hydrides ($\text{HM}'_x(\text{CO})_y$) to produce $[\text{Cp}_2\text{MoH}(\text{CO})]\text{M}'_x(\text{CO})_y$ and H_2O . The reactivity of transition metal hydrides towards **1** follows the trend of the metal hydride's acidity, i.e., $\text{HCo}(\text{CO})_4 > \text{H}_2\text{Fe}(\text{CO})_4 \gg \text{HMCP}(\text{CO})_3, \text{Cp}_2\text{MoH}_2$. The capability of the hydrides $\text{HCo}(\text{CO})_4$ and $\text{H}_2\text{Fe}(\text{CO})_4$ to be produced from molecular hydrogen raises the attractive possibility of their serving as agents for catalytic CO_2 reduction. Studies were initiated on modeling CO_2 insertion reactions into M-C bonds using $(\text{MeC}_5\text{H}_4)_2\text{Nb}(\eta^2\text{-CO}_2)\text{CH}_2\text{SiMe}_3$ (**2**), the only established example of a complex containing both CO_2 and alkyl ligands. Surprisingly, **2** undergoes decarbonylation rather than insertion when heated at 60°C , efficiently producing the oxo complex $(\text{MeC}_5\text{H}_4)_2\text{Nb}(\text{O})\text{CH}_2\text{SiMe}_3$. Furthermore, this decarbonylation is dramatically accelerated by ultraviolet irradiation. Recent efforts to promote insertion reactions of **2** are centered on reactions with Lewis acids and external ligands. Finally, a series of remarkable rhodium-catalyzed H-transfer reductions of CO_2 to formic acid under very mild conditions was discovered. Either H_2 or H-donor substrates (e.g., ethers) can serve as reductants. In the latter mode added O_2 induces substrate oxidation with concomitant CO_2 reduction. Studies to elucidate and expand these novel initial results are under way. A number of new systems are also under investigation including the thermal and photochemical reactions of $\text{Mo}(\text{CO})_2(\text{PMe}_3)_4$ and $(\text{R}_3\text{P})_2\text{Ni}(\text{CO}_2)$.

University of Oregon Eugene, OR 97403

Department of Chemistry

295. Polyoxyanion-Mediated Methane Activation and Functionalization: Molecular

Design of New Homogeneous and New Solid-State/Heterogeneous Catalysts

Finke, R.G.

\$85,375

Comm. 503-346-4622

The goal of this research is to develop a chemical paradigm for polyoxoanion-supported transition-metal catalysis, with an emphasis on small molecule (hydrogen, oxygen, and methane) catalytic activation and hydrocarbon functionalization (methane, other alkanes). Kinetic and mechanistic studies are an integral part of this work, since they provide both the best and fastest way to reliably establish the strengths and weaknesses of this previously unknown class of catalytic materials. The first example of a polyoxoanion-supported catalyst has been reported. That work employs the novel, second-generation catalyst precursor $[(\text{Bu}_4\text{N})_5\text{Na}_3][(\text{1,5-COD})\text{Ir-P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$, the best polyoxoanion-support material to date, and describes hydrogen and olefin activation and related chemistry. A mechanistic study, providing the needed evidence that the true catalyst is indeed polyoxoanion-supported, has also been reported. The mechanistic studies pointed toward a preference for oxidative addition of substrates like hydrogen and oxygen, and led to studies of cyclohexene catalytic oxidations by oxygen and $[(\text{Bu}_4\text{N})_5\text{Na}_3][(\text{1,5-COD})\text{Ir-P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$. This work provides the first example of oxidative catalysis by a polyoxoanion-supported metal and only the second example of polyoxoanion-supported catalysis of any type. The turnover rates and turnover numbers are better than any previous Ir-catalyzed oxygenation of cyclohexene using dioxygen.

**Pennsylvania State University, University Park
University Park, PA 16802**

Department of Chemical Engineering

296. Enhancement of Activity and Selectivity by Metal-Support Interactions

Vannice, M.A.

\$111,418

Comm. 814-863-4803

The project objectives are (1) to elucidate the chemistry involved in the creation of metal-support interactions that have a pronounced influence on adsorption and catalytic behavior and (2) to use these effects to favorably alter hydrogenation reactions. Focus is on characterizing adsorbed molecules and the chemical and physical state of the metal and support. Early studies found rate enhancements greater than 100-fold for CO and acetone hydrogenation (to isopropyl alcohol), and an increase in selectivity from zero to over 35% for crotyl alcohol formation from crotonaldehyde, rather than butyraldehyde, when titania was used to disperse Pt. A model invoking special active sites at the metal-support interface has been proposed to explain this behavior. It is now being tested further by studying the selectivity of acetophenone hydrogenation over Pt. A study of Au/TiO₂ catalysts has been completed which investigated whether Frost's model invoking O vacancies on the titania surface could explain this behavior. It cannot, because these catalysts were inactive in these hydrogenation reactions, but they were found

to be excellent CO oxidation catalysts at 300 K. An ultra-high vacuum (UHV) system with high-resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS), and a high-pressure reaction chamber is now ready to investigate CO and acetone adsorbed on Pt and TiO₂ single crystals and a Pt-covered TiO₂ single crystal. Studies of the benzene-toluene-xylene system (BTX) have shown that turnover frequencies (TOFs) on Pd can be increased using acidic supports. The addition of methyl groups to the ring decreases TOF values in the order benzene > toluene ≥ p-xylene ≥ m-xylene > o-xylene. The presence of additional acidic adsorption sites on the support near the Pd crystallites has been proposed to explain this behavior, and Pt is now being studied. Characterization of these adsorbed molecules using infrared spectroscopy can also be accomplished if time permits.

Department of Chemistry

297. Mechanistic Studies of Carbon Monoxide Insertion into Metal-Nitrene and Metal-Carbene Bonds

Geoffroy, G.L.

\$113,256

Comm. 814-865-9591

The overall goal of this proposed work is to develop a detailed understanding of the manner in which small organic ligands can be elaborated into more complex ligands by a variety of metal-mediated carbon-carbon, carbon-nitrogen, and carbon-oxygen bond forming reactions using highly nucleophilic acetylide, vinyl, and vinylidene complexes. Preliminary studies have shown that anionic acetylide complexes of the type $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Mn-C}\equiv\text{CR}]^-$, **1**, can be prepared and that they undergo a series of unusual addition and cycloaddition reactions with heterocumulenes, vinylketones, and epoxides. The acetylide complex **1** is chiral, and the stereochemistry at the metal has been observed to strongly influence the stereochemistry of the new organic ligand formed in these transformations. These studies are being extended by examining the reactivity of complex **1** with an extensive variety of other organic substrates and also by exploring its reactivity with a series of electrophilic organometallic complexes. The latter reactions have the potential to form bimetallic complexes with completely new types of bridging organic ligands. Effort is also being devoted to resolving the carbene complex $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Mn-C}(\text{OR})\text{R}'$, the precursor to **1**, into its separate enantiomers so that complex **1** can be prepared enantiomerically pure and then used in highly stereospecific transformations. Other studies in progress are aimed at developing methodologies for the high-yield demetallation of the organometallic carbene and vinylidene products of the reactions of **1** with organic substrates, so that the free organic products containing the new chiral centers can be smoothly obtained in high yield. Preliminary experiments indicate that anionic and highly nucleophilic vinyl and vinylidene complexes of the types $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Mn-C}(\text{R})-\text{CR}_2]^-$ and $[\text{Cp}(\text{CO})_2\text{W}=\text{C}=\text{CHR}]^-$ can be prepared, and experiments are planned to explore the reactivity of these complexes with a variety of organic and organometallic complexes to define the nucleophilicity of the complexes and, in the former case, their potential use in stereospecific organic synthesis.

298. Transition-Metal-Mediated Transformations of Small Molecules

Sen, A. **\$90,700**
Comm. 814-863-2460

The catalysis of organic transformations by transition metals, especially in solution, is of great practical and scientific importance because of the high efficiency, high specificity, and low energy demands often associated with these systems. The project objectives are: (1) to achieve a fundamental understanding of a number of important processes of this type and (2) to use this knowledge to develop new and useful catalytic processes. The project encompasses research in two specific areas of catalysis. The first involves the catalytic synthesis of new alternating copolymers of carbon monoxide with olefins, as well as new catalytic routes to polyureas and polyoxamides. Such polymers have many potential practical applications. The second area of research is concerned with the development of novel hybrid catalyst systems involving both homogeneous and heterogeneous components for the oxidation of alkanes. Alkanes are the most abundant and the least reactive members of the hydrocarbon family and their selective, catalytic oxidation under mild conditions is one of the most challenging chemical problems, in addition to being of great practical importance.

Department of Materials Science and Engineering

299. Determination of the Distribution of Hydrogen in Coal by Fourier Transform Infrared (FTIR) Spectroscopy

Painter, P.C. **\$98,600**
Comm. 814-865-5972

The purpose of this research is to determine the role of hydrogen-containing functional groups in coal. The work consists of two interrelated parts: (1) the quantitative determination of the aliphatic and aromatic CH content by Fourier transform infrared (FTIR) spectroscopic measurements and (2) the application of a newly developed thermodynamic model that describes the role of hydrogen bonding interactions. This research is aimed at providing fundamental knowledge of coal structure both at the level of local composition and at the larger scale of the effect of the balance of intermolecular forces on solution and swelling behavior. In recent work previous methods of relating swelling measurements have been modified to account for hydrogen bonding and the treatment has been extended to include equation of state or free volume effects. The spectroscopic studies have now culminated in the determination of absorption coefficients for the aliphatic and aromatic CH stretching modes.

**University of Pennsylvania
Philadelphia, PA 19104-6393**

Department of Chemical Engineering

300. Support Effects Studied on Model Supported Catalysts

Gorte, R.J. **\$90,800**
Comm. 215-898-4439

Model catalysts consisting of thin films of Group VIII metals deposited on alumina, zirconia, and zinc oxide substrates are being used to study the properties of supported metal catalysts. Samples are prepared under ultrahigh vacuum conditions and can be characterized using standard surface science techniques, including Auger electron spectroscopy, photoelectron spectroscopy, and temperature-programmed desorption of simple gases. Transmission electron microscopy is being used to characterize selected samples, and reaction rates for CO hydrogenation and NO reduction by CO are being used on some samples to relate the spectroscopic results to the catalytic properties. Preparation conditions and metal loading are being varied in order to separate effects caused by oxide and particle size. The results of these experiments are being used to understand how the oxide substrate affects the structure and properties of supported metal particles.

Department of Chemistry

301. Catalytic Synthesis of Silicon Carbide Pre ceramic Polymers: Polycarbosilanes

Berry, D.H. **\$123,011**
Comm. 215-898-2705

The first homogeneous transition metal catalysts for the dehydrogenative coupling of simple alkyl silanes to oligomeric and polymeric carbosilanes, $H-(SiR_2CR'_2)_n-SiR_3$, have been developed and are under investigation. Polycarbosilanes are the most successful and widely studied class of polymer precursors for silicon carbide, but traditional methods for their synthesis are inefficient and nonselective. Well-characterized ruthenium complexes of the type $(PR_3)_3Ru(H)_2(SiR'_3)$ catalyze the dehydrogenation of trialkyl silanes at 150°C to produce a distribution of linear and branched carbosilanes. Initial results suggest that transient metal silaolefin complexes of the type $L_nRu(\eta^2-R_2Si=CR'_2)$ play a key role in the catalytic silane dehydrogenation and carbosilane formation. The silaolefin complexes appear to be generated by β -hydrogen elimination from silyl ligands, and subsequent net addition of Si-H bonds across the coordinated silaolefin leads to Si-C bond formation, in direct analogy to the hydrosilylation of organic olefins. Current studies include detailed elucidation of the catalytic mechanism and development of more active catalyst systems.

302. Synthesis and Properties of New Pre ceramic Materials

Sneddon, L.G. **\$103,000**
Comm. 215-898-8632

The goal of this project is to develop new selective high yield synthetic routes to important solid-state materials that allow the production of these materials in forms, such as fibers, coatings, or shaped bodies, unattainable

using conventional synthetic techniques. Because of their importance in both electronic and structural applications, boron-based ceramic materials, including boron carbide, boron nitride, and metal borides are materials of particular focus. Several new boron-polymer systems have been produced, including poly(vinylborazine), poly(vinylpentaborane), and poly(borazylene), that have proven to be high-yield processable precursors to boron carbide and/or boron nitride. Other recent work has resulted in the development of a new composite polymeric precursor system to titanium and zirconium diborides. The use of these new chemical precursor systems for the formation of coated materials, such as boron nitride coatings for use in ceramic matrix composites and TiB₂ coatings for use in metal matrix composites, is also being explored.

303. Catalytic Hydrogenation of Carbon Monoxide

Wayland, B.B.

\$118,000

Comm. 215-898-8633

Rhodium porphyrin and related macrocycle complexes are being used to probe the formation of intermediates in several pathways for the hydrogenation of carbon monoxide. Favorable thermodynamic factors for producing both formyl complexes (M-CHO) from H₂ and CO and reductive coupling of CO to form α -diketone species (M-C(O)C(O)-M) provide an unusual opportunity to evaluate these types of complexes as productive intermediates in organic oxygenate formation. Metal promoted reactions of CO and H₂ to form intermediate metalloformyl (M-CHO) and hydroxymethyl (M-CH₂OH) complexes is the most widely accepted route to organic oxygenates. Alternate pathways that utilize reductive coupling of CO as the initial step and subsequent hydrogenation may be important in selective formation of two carbon products. Rhodium macrocycle complexes are currently unique in accomplishing formation of the primary intermediates in these divergent CO hydrogenation mechanisms. Studies are directed toward the use of nonmacrocyclic ligand complexes that emulate the favorable thermodynamic features associated with rhodium macrocycles, but that also manifest improved reaction kinetics. Multifunctional catalyst systems designed to couple the ability of rhodium complexes to produce formyl and diketone intermediates with a second catalyst that hydrogenates these intermediates are being evaluated as candidates to accomplish CO hydrogenation at mild conditions.

University of Pittsburgh
Pittsburgh, PA 15260

Department of Chemistry

304. Studies of Supported Hydrodesulfurization Catalysts

Hercules, D.M.

\$100,000

Comm. 412-624-8300

The overall objective of the research is to develop a spectroscopic methodology for the study of catalyst surfaces and to establish a surface structure/activity relationship. Ion scattering spectroscopy has been used for monitoring the surface coverage of Mo/Al₂O₃ catalysts. By modeling changes in the ISS Mo/Al intensity ratio as a function of

Mo coverage it was shown that for Mo/Al₂O₃ catalysts prepared by equilibrium adsorption, coverage of the alumina surface should be complete at a loading of 55 x 10¹³ atom/cm². This value agrees with that obtained from modeling of the ISS Al/O intensity ratio as a function of Mo loading. The activity of reduced Mo/Al₂O₃ catalysts (8 wt % Mo) for propane hydrogenolysis has been studied as a function of the reduction temperature. The results were correlated with the distribution of Mo oxidation states in the reduced catalysts measured by X-ray Photoelectron Spectroscopy (XPS, ESCA). Catalysts containing Mo oxidation states higher than Mo⁺² were not active for propane hydrogenolysis. The onset of catalytic activity appears to coincide with Mo⁺² formation. A sharp increase in the catalytic activity was however observed at the reduction temperature where Mo metal first appears (ca. 700°C). The variation of the catalytic activity was similar to that of the abundance of Mo metal.

305. Vibrational Spectroscopic Studies of Surface Chemical Interactions in Chemisorption and Catalysis

Yates, J.T., Jr.

\$153,000

Comm. 412-624-8320

This research is concerned with the use of vibrational spectroscopy for the study of elementary surface processes of importance in understanding catalysis by metals and by chemically modified metal surfaces. The vibrational spectroscopic methods employed include Fourier transform (FT)-infrared reflection absorption spectroscopy, high-resolution electron energy loss spectroscopy, and transmission infrared spectroscopy, with the latter method being employed to study actual high surface area catalysts. Current problems include: (1) the activation and poisoning of CO-based and N₂-based surface chemistry; (2) the influence of electric fields on CO bonding to metals; (3) the thermal activation of methane, discriminating between activation of weakly bound methane and activation of methane in the gas phase above the surface; (4) fundamental studies of ethylene chemistry on supported Pt; and (5) fundamental studies of the metal-support interaction on both real and model metal catalysts supported on Al₂O₃ and SiO₂. Both high resolution electron energy loss spectroscopy (HREELS) and transmission IR spectroscopy are employed in this work.

Purdue University
West Lafayette, IN 47907

Department of Chemistry

306. Fundamental Studies of Reactive Intermediates in Homogeneous Catalysis

Squires, R.R.

\$100,000

Comm. 317-494-7322

The thermochemical properties and intrinsic reactivity of organometallic species relevant to homogeneous catalysis are being investigated with use of a tandem flowing after-glow triple quadrupole instrument. This device enables the formation and isolation of reactive transition metal containing ions in the gas phase by a variety of methods, including electron ionization of volatile organometallic complexes, and *in situ* synthesis of new metal ions from simpler precursors. The instrument is being outfitted with

an electrospray ionization source which will allow direct sampling of preformed organometallic ions from homogeneous solutions, including catalytically active solutions. The structures, physical properties, and chemical behavior of the gaseous metal ions are being characterized through kinetic and product distribution measurements, and by energy-resolved collision-induced dissociation (CID) experiments. An extensive series of metal ligand bond strengths have been determined from CID threshold energy measurements, including sequential M-CO bond energies in anionic and neutral transition metal carbonyls, M-(η^2 -CO₂) and M-($\eta^{1,2}$ -O₂) bond energies in dioxygen activation intermediates, and metal ligand bond energies in various organometallic anions. The activation energies for decarboxylation and decarbonylation of metal hydroxycarbonyls L_nMCOOH, metal formates L_nM(O₂CH), metal formyls L_nMCHO, and metal hydrides L_nMH are being determined in order to construct reaction-energy profiles for homogeneously catalyzed CO- and CO₂-activation cycles.

Rensselaer Polytechnic Institute Troy, NY 12180

Department of Chemistry

307. *Selective Transformations of Carbonyl Ligands to Organic Molecules*

Cutler, A.R.

Comm. 518-276-8447

Efforts have been directed toward synthesizing (η^5 -indenyl)(PPh₃)(CO)Ru-CH(OR)R' complexes (R = Me, Et, SiHPh, SiHEt₂; R' = H, CH₃), which are being characterized. The diastereoselectivity that is observed as they form, by reduction of alkoxy-carbenes [Ru] = C(OR)CH₃⁺ and by catalyzed hydrosilylation of [Ru]-COCH₃, is of particular interest. Indenyl ruthenium complexes (η^5 -indenyl)(L)(CO)Ru-R'' (L = CO, PPh₃) in general add CO under extremely mild conditions and afford stable (η^5 -indenyl) Ru acyl complexes. Rh(I) complexes, including (PPh₃)₃RhCl, and (PPh₃)(CO)₄MnCOCH₃ are particularly effective hydrosilylation catalysts for adding R₂SiH₂ (R = Et, Ph) across the acetyl complexes L_xM-COCH₃ (L_xM = Cp(PR₃)(CO)Fe, Cp(PR₃)(CO)Ru) and (indenyl)(PPh₃)(CO)Ru(PR₃; R = OMe, OPh, Ph, Et). The resulting siloxyethyl ruthenium complexes are stable and are fully characterized, whereas the labile iron congeners degrade to their vinyl derivatives Cp(PR₃)(CO)Fe-CH = CH₂. "Noncatalyzed" hydrosilylation of the manganese acyls (CO)₅Mn-COCH₂R (R = H, OCH₃, CH₃) occurs at ambient conditions with the monohydrosilanes Et₃SiH, Me₂EtSiH, Me₂PhSiH, Ph₃SiH, and Me₂ClSiH, although several competing pathways are evident. For example, (CO)₅MnCOCH₃ adds Me₂PhSiH or Me₂ClSiH to give fully characterized siloxyethyl complexes (CO)₅Mn-CH(OSiXMe₂)CH₃, incorporates Et₃SiH (one equiv.) to provide the siloxyvinyl systems (CO)₅Mn-C(OSiEt₃) = CH₂, and consumes Ph₃SiH to give (CO)₅Mn-CH₂CH₃ plus (Ph₃Si)₂O. Continuing mechanistic studies have focused on the reactions of monohydrosilanes R₃SiH with manganese (CO)₅MnCOR and with cobalt (CO)₃(PR₃)CoCOCH₃ acyl complexes, as well as the use of these cobalt and manganese systems as catalysts for hydrosilylating Cp(CO)₂FeCOCH₃. Efforts to develop a phosphide-phosphine "switch" for controlling the reactivity (and stereochemistry) of

acyl ligand reduction on Cp(PPh₂H)(CO)FeCOCH₃/Cp(PPh₂)(CO)FeCOCH₃⁻¹ recently have involved characterizing the products of treating the latter anion with R₃SiCl, Cp(CO)FePPh₂C(CH₃)OSiPh₃, and with FpCl Fp-PPh₂-Fe(CO)Cp(COCH₃).

University of Rochester Rochester, NY 14627

Department of Chemistry

308. *Transition Metal Activation and Functionalization of Carbon-Hydrogen Bonds*

Jones, W.D.

\$110,000

Comm. 716-275-5493

The investigation of homogeneous C-H bond activation by (C₅Me₅)Rh(PMe₃) has been continued. Earlier studies have shown that the increased stability of metal phenyl hydride complexes relative to metal alkyl hydride complexes can be attributed to the stronger metal-phenyl bond. Other aromatic C-M bonds are also found to be strong. The preference for (C₅Me₅)Rh(PMe₃)(2-furyl)H over an η^2 -furan complex indicates that the aromaticity of the group activated may play an important part in the strength of the carbon-metal bond. A variety of new η^2 -arene complexes of the type (C₅Me₅)Rh(PMe₃)(η^2 -arene) where the arene is a fused, polycyclic aromatic has been discovered. The dynamics of the η^2 -arene to aryl hydride interconversions are being examined, as are the electronic effects upon the site of η^2 -binding. It has also been found that thiophene undergoes selective C-S bond cleavage via insertion of the metal. Mechanistic studies suggest that the insertion reaction proceeds by way of initial S-coordination. A series of RhCl(PR₃)₂(CNR) complexes catalyze the insertion of isonitrile into aromatic C-H bonds. Light is used to dissociate an isonitrile ligand from the complex, and low concentrations of added isonitrile are used to increase efficiency. The reaction is believed to occur by way of initial phosphine dissociation.

Rutgers University Piscataway, NJ 08855-0939

Department of Chemistry

309. *Carbon-Hydrogen Bond Functionalization Catalyzed by Transition Metal Systems*

Goldman, A.S.

\$75,000

Comm. 201-932-5232

Significant progress has been made toward the goals of developing and understanding rhodium-based systems for catalytic alkane functionalization reactions including (1) dehydrogenation and (2) carbonylation. The starting point for this work was the discovery that Rh(PMe₃)₂(CO)Cl photochemically catalyzes both of these alkane reactions. In addition, it was found that transfer-dehydrogenation of alkanes (using alkenes as sacrificial hydrogen acceptors) can be photocatalyzed. The mechanisms of both the photodehydrogenation and the phototransfer-dehydrogenation were elucidated. In both cases formation of the fragment Rh(PMe₃)₂Cl is the only photochemical

step. These mechanisms implied that $\text{Rh}(\text{PMe}_3)_2(\text{CO})\text{Cl}$ should act as a thermal alkene hydrogenation catalyst under sufficiently high H_2 pressures. Reductive elimination of the hydrogenated alkane product should afford the key fragment, $\text{Rh}(\text{PMe}_3)_2\text{Cl}$, which could then react further to dehydrogenate alkane. In fact, under high H_2 pressures alkane transfer-dehydrogenation is thermally catalyzed with turnover numbers and rates far greater than those previously reported systems, e.g., 1000 catalytic turnovers/h at 80°C . It has also been found that photochemical $\text{Rh}(\text{PMe}_3)_2(\text{CO})\text{Cl}$ -catalyzed alkane carbonylation is cocatalyzed by aromatic carbonyls (ketones and aldehydes); quantum yields 200 times greater than in the absence of the added carbonyls have been achieved in some cases. Thermal carbonylation systems will continue to be explored based on the stratagem of developing aldehyde decarbonylation catalysts which are not suppressed by CO atmosphere.

Department of Physics and Astronomy

310. Structure and Reactivity of Model Thin Film Catalysts

Madey, T.E. **\$91,200**
Comm. 908-932-5185

The relationship between microscopic surface structure and chemical reactivity is being studied for model bimetallic catalysts (i.e., ultrathin films of metals on metals). The focus of the work is on atomically rough unstable single-crystal surfaces that undergo massive reconstruction and faceting when covered with certain ultrathin metal films (≈ 1 monolayer thick), upon annealing to elevated temperatures. Such surfaces include the bcc(111) and the fcc(210) surfaces. Present studies are focused on ultrathin films of Pd, Pt, and Au on the W(111) surface. This film-covered surface reconstructs to form microscopic facets upon annealing to $T > 800$ K. Both LEED and scanning tunneling microscopy (STM) are used to characterize surface morphology. In contrast, ultrathin films of Ni on W(111) do not induce faceting. Current studies are concentrated on characterizing the adsorption behavior and catalytic activity of these films in order to determine the effect of adsorption and reaction on the stability of ultrathin metal films on W. Future studies will focus on the growth, thermal stability, and reactivity of metal films on atomically rough surfaces of fcc and hcp metals.

University of South Carolina Columbia, SC 29208

Department of Chemistry

311. The Transformations of Organic Amines by Transition Metal Cluster Compounds

Adams, R.D. **\$108,460**
Comm. 803-777-7187

The current objective is to study the nature of the chemical transformations of unsaturated hydrocarbons that have amine containing substituents by metal cluster complexes. The principal objectives are to determine: (1) the nature of C-H and C-N bond cleavage and bond formation processes at multinuclear metal sites and (2) the nature of the coordination and reactivity of activated

amines in metal cluster complexes and the relationship of these to the bond transformation processes. Additional studies are focused on reactions of cluster complexes containing activated amine ligands with hydrogen for the purpose of characterizing important hydrogenation and hydrogenolysis reactions. The reactions of ynamines with CO ligands to produce the activation and splitting of the CO bond by metal cluster complexes is also under study.

University of Southern California Los Angeles, CA 90089-0482

Department of Chemistry

312. Chemistry of Bimetallic and Alloy Surfaces

Koel, B.E. **\$119,500**
Comm. 213-740-4126 **(18 months)**

This research is focused on elucidating the underlying principles that govern chemical reactions occurring on bimetallic and alloy surfaces. This understanding will aid in the atomic level explanation of the reactivity and selectivity of alloy and bimetallic cluster catalysts and will be important for the design of new catalysts with improved performance. Using a battery of surface science methods, fundamental data on the thermochemistry, and kinetics of the adsorption and reaction of molecules on extensively characterized, single-crystal bimetallic surfaces will be obtained. Changes in chemisorption bond strengths, adsorption site distributions, and hydrocarbon fragment stability and reactivity are correlated with the geometric and electronic structure of the metal atoms on the surface. Careful design of experiments can isolate factors (e.g., ensemble and ligand effects) that control surface chemistry and catalysis on bimetallic and alloy surfaces. Alkali promoters strongly affect the reactions of hydrocarbons on Pt and Ni surfaces by altering the electronic structure and inducing significant site-blocking effects. Bismuth coadsorption provides benchmark data on ensemble sizes required for chemical reactions on Pt and Ni surfaces. Surface alloys, for example Sn/Pt, are used for detailed probing of ensemble sizes and also reactive site requirements.

Southern Illinois University Carbondale, IL 62901-4709

Department of Chemistry

313. Studies of the Stabilities and Reactions of Solution Phase Organic Radicals

Bausch, M. **\$137,000**
Comm. 618-453-6461 **(18 months)**

The project objective is to develop a more complete understanding of the stabilities and reactions of relatively large (molar mass > 100 g) organic radicals. Specifically, the research will aid in clarifying factors that affect the thermodynamic and kinetic stabilities of selected organic radicals, probe the acidic nature of organic radicals and the stabilities of their respective radical anionic conjugate bases, and determine bond strengths in organic radicals and radical anions. Analyses of the data that result from

completion of these experiments will enable formulation of new hypotheses that should more accurately rationalize the formation and subsequent reactions of organic radicals, and add new insights into the understanding of chemical reactions associated with the combustion and conversion of fossil fuels. Many of the data in this study will be collected with the aid of colorimetric and electrochemical protocols. Of particular interest is the use of high-speed cyclic voltammetric techniques in evaluations of the solution phase kinetics of carbon-centered radical dimerizations.

**Stanford University
Stanford, CA 94305-5025**

Department of Chemical Engineering

314. Catalyzed Gasification of Tungsten and Tungsten Carbide Catalysts

Boudart, M.

\$85,000

Comm. 415-723-4748

The use of ^{129}Xe NMR as a probe of catalytic surfaces has been explored. The sample was in the form of a few large pellets of platinum clusters supported on silica, or alumina. The average size of the platinum clusters in the different samples ranged from 1.5 to 8 nm. When successive doses of H_2 are chemisorbed at 450 K on the prerduced and evacuated samples, the NMR spectrum consists of one line, with the value of chemical shift, δ , shifting to lower values with successive doses. However, the slope of the decrease in δ with successive doses of H_2 changes for a surface coverage, θ , ~ 0.3 , irrespective of the metallic particle size or the support. Thus, ^{129}Xe NMR is sensitive to changes in the structure of the platinum surface upon chemisorption of H_2 . However, the value of δ extrapolated to $\theta = \text{zero}$, depends on the support. Thus, for silica supported platinum, the extrapolated δ coincides with the measured value of δ of the reduced and evacuated sample. On the other hand, the extrapolated δ with θ for platinum on alumina is higher than the measured δ of the reduced and evacuated sample. These results suggest that the metal-support interaction differs for platinum on silica or alumina. In this way, although qualitative, ^{129}Xe NMR is a valuable, easy-to-use technique to probe changes on the surface of supported metals, as well as on the interaction of metals and the support. This information, difficult to obtain otherwise, is important to catalysis, and further applications of the ^{129}Xe NMR technique are being explored.

315. Molecular Beam Studies of Activated Adsorption and Heterogeneous Kinetics on Transition Metal Surfaces

Madix, R.J.

\$139,685

Comm. 415-723-2402

Adsorption of gases on metal surfaces is the first step in heterogeneous catalysis. Activated adsorption on clean surfaces may proceed either by a direct collisional process, in which bonds within the molecule are broken during a collisional lifetime of approximately 10^{-12} seconds, or via longer-lived trapped states which allow the molecule to probe the surface for more reactive configurations. Because of the broad distribution of kinetic energies in the

Boltzmann distribution, both routes may contribute to reaction. Simple theories treat the trapping process as one dimensional, assuming that the momentum of the molecule parallel to the surface is conserved in the energy exchange process. This research has shown that such treatments do not adequately describe the dependence of adsorption on kinetic energy for xenon, methane, and ethane. In each case tangential momentum plays an important role in the trapping process. The degree to which these processes involve tangential momentum can be expressed in terms of the manner in which they scale with $E_T \cos^n \Phi$, where E_T is the total kinetic energy of the incident molecule, Φ is the angle of incidence with respect to the surface normal, and n is the scaling parameter. A value of n equal to two is expected for the one-dimensional models. For xenon, methane, and ethane on Pt(111) the values of n observed are 1.0, 0.6, and 0.6, respectively. Trajectory simulations for xenon indicate that substantial roughness of the surface potential along the surface leads to adsorption at energies far above the cutoff imposed by the one-dimensional models. Since catalytic reactions often proceed in the presence of unreactive surface residues, the effect of adsorbed species on the dynamics of adsorption was also examined. The trapping probabilities, S' , for both xenon and ethane on the Pt(111) surface which has been presaturated with the gas is higher than that on the clean surface, S_0 , at all kinetic energies, reflecting the high efficiency of energy exchange between the incident and the weakly bound molecule. Furthermore, in both cases the trapping probability scales with the total energy ($n = 0$), in striking contrast to the behavior on the clean surface. These results suggest that trapping is dominated by processes which couple normal and tangential momentum efficiently on the covered surface. Overall, the trapping probabilities measured on the saturated monolayer can be used to describe the increase in the trapping probability that accompanies increasing coverage of the adsorbate, according to $S = S_0(1 - \Theta) + S'\Theta$.

State University of New York at Binghamton

Binghamton, NY 13902-6000

Department of Chemistry

316. Photochemistry of Intermolecular C-H Bond Activation

Lees, A.J.

\$78,000

Comm. 607-777-2362

The project objective is to elucidate the photochemistry of metal carbonyl complexes which activate intermolecular hydrocarbon C-H bonds. The complexes studied include $(\eta^5\text{-C}_5\text{R}_5)\text{M}(\text{CO})_2$ ($\text{M} = \text{Rh, Ir; R} = \text{H, Me}$), $(\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\text{CO})_2$ ($\eta^5\text{-C}_9\text{H}_7 = \text{indenyl}$), and $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{L}$ ($\text{L} = \text{a pyridine derivative}$). Low-temperature spectroscopic and steady-state laser photolysis measurements have been performed under dilute conditions in deoxygenated alkane and aromatic solvents. For each system the solution photoreaction has been carefully monitored by diode-array uv-visible and FTIR spectroscopy and photoproducts have been further characterized by mass spectrometry. The solution photochemistry of $(\eta^5\text{-C}_5\text{R}_5)\text{Rh}(\text{CO})_2$ ($\text{R} = \text{H, Me}$) has also been

monitored in the presence of excess PPh_3 scavenging ligand at various excitation wavelengths. FTIR spectral sequences recorded over the time of photolysis illustrate that these photoreactions involve clean and complete conversion to the $(\eta^5\text{-C}_5\text{R}_5)\text{Rh}(\text{CO})(\text{PPh}_3)$ products. Photochemical quantum efficiencies have been determined and in each case they show a linear dependence on entering PPh_3 ligand concentration in the 0.05 to 0.3 M range, indicating that these reactions involve a photosubstitution mechanism. The photochemistry of $(\eta^5\text{-C}_5\text{R}_5)\text{Rh}(\text{CO})_2$ in Et_3SiH solution has also been studied to determine the nature of the Si-H activation processes. In these cases the observed photochemical quantum yields are independent of Et_3SiH concentration, illustrating a dissociative photochemical process. These results, taken together, lead to postulated models for the nature of C-H and Si-H activation and ligand substitution. Studies are under way to determine the absolute photochemical efficiencies of various metal complexes that facilitate intermolecular C-H bond activation.

State University of New York at Buffalo
Buffalo, NY 14214

Department of Chemistry

317. Mechanistic Examination of Organometallic Electron-Transfer Reactions
Atwood, J.D. **\$82,825**
Comm. 716-831-2122

Research is focused on the understanding of oxidation state changes for organometallic complexes. Broadly, oxidation state changes can be separated into those that involve a two electron change accompanied by the transfer of an atom or group and those that involve transfer of one electron. Research centering on reactions of metal carbonyl anions has demonstrated both types of reactions. Reactions that involve a formal two electron change have been observed when a more nucleophilic metal carbonyl anion abstracts a group (CO^{2+} , H^+ , or CH_3^+) from a less nucleophilic metal carbonyl anion. These reactions occur rapidly, with H^+ transfer more rapid than CH_3^+ or CO^{2+} transfer. The rate of these group transfer reactions is related to the difference in nucleophilicity between the reactant and product metal carbonyl anions. The single electron transfer reactions of metal carbonyl anions lead to odd-electron complexes with rates that correlate reasonably with the driving force for the reaction. The resulting reactions (ligand scrambling, hydrogen abstraction, and combination) are typical for odd-electron complexes. With these studies of electron-transfer reactivity, an important reaction type for organometallic complexes and in catalysis, a foundation for understanding is being developed.

Texas A & M University
College Station, TX 77843-3255

Department of Chemistry

318. Correlations Between Surface Structure and Catalytic Activity/Selectivity
Goodman, D.W. **\$180,500**
Comm. 409-845-0214

This project involves an investigation of the issues that are keys to understanding the relationship between surface structure and catalytic activity/selectivity. A strong emphasis is placed on the origins of the special properties of mixed-metal catalysts. The experimental approach utilizes a microcatalytic reactor contiguous to a surface analysis system, an arrangement which allows *in vacuo* transfer of the catalyst from one chamber to the other. Surface techniques being used include Auger (AES), uv and X-ray photoemission spectroscopy (UPS and XPS), temperature programmed desorption (TPD), low-energy electron diffraction (LEED), high-resolution electron energy loss spectroscopy (HREELS), and Fourier transform infrared spectroscopy (IRAS). The project objectives are (1) the investigation of the unique catalytic properties of ultrathin metal films with emphasis on methanol synthesis and carbon monoxide oxidation over monolayer copper and palladium films on rhodium; (2) the understanding of the nature of the electronic modification found in metal overlayer systems compared to their bulk analogs and the relationship of the perturbations to the special chemistry exhibited by these systems; and (3) the simulation of supported metal catalysts using metal deposits on thin oxide films, e.g., Ni, Cu, onto a well-characterized thin oxide film of the support material, e.g., Al, Si, Mg.

319. Catalysts and Mechanisms in Synthesis Reactions
Lunsford, J.H. **\$103,300**
Comm. 409-845-3455

The objective of this research is to understand the role of surface-generated gas-phase radicals in catalytic oxidation of hydrocarbons, with emphasis on the conversion of methane to more useful chemicals and fuels. Both matrix isolation electron spin resonance (MIESR) and laser-induced fluorescence (LIF) methods have been used to detect radicals that emanate from a hot metal oxide or metal surface during a catalytic reaction. Reactions of methyl radicals with metal oxide powders have been studied quantitatively for the first time in an attempt to understand the very large differences in selectivity that occur during the catalytic oxidation of methane. The probability that a methyl radical reacts upon colliding with a surface decreases from 10^{-5} for ZnO to 10^{-7} for MgO. With the more reactive oxides electrons are transferred from the methyl radicals to the metal ions, and methoxide ions are formed on the surface. At high temperatures these methoxide ions are intermediates in the nonselective oxidation of methane to carbon monoxide and carbon dioxide. In a separate set of experiments hydroxyl radicals have been observed during the oxidation of methane or hydrogen over platinum wires. Preliminary results indicate that the hydroxyl radicals are formed from water, which is a product of the oxidation reaction, but the other components are essential for maintaining a proper level of oxygen on the surface.

University of Texas at Austin
Austin, TX 78712-1062

Department of Chemical Engineering

320. Model Catalytic Oxidation Studies Using Supported Monometallic and Heterobimetallic Oxides

Ekerdt, J.G.

\$76,400

Comm. 512-471-4689

This research program is directed toward developing a fundamental understanding of how catalyst composition, redox ability, and structure control the catalytic properties of metal oxides. Oxide systems that permit the examination of the role of metal oxide cations separately and in pairwise combinations are being developed. Organometallic complexes containing allyl, benzyl, cyclopentadienyl, or carbonyl ligands are exchanged with the hydroxide ligands of silica, alumina, titania, zirconia, and magnesia supports. The exchange technique is used to achieve high metal oxide loadings without the formation of supported crystallites. The supported complex is subsequently oxidized to generate a supported oxide. Isolated anions, such as MoO_4^{2-} , and polyanions, such as $\text{Mo}_7\text{O}_{24}^{6-}$, form from these precursors when the oxides are maintained in an ambient environment and isolated structures, such as MoO_6 , are formed under anhydrous conditions. Monometallic complexes of Mo, W, Cr, Ti, Zr, and Nb, and heterobimetallic complexes of MoW are being used to prepare supported metal oxides. The research involves characterization of the organometallic deposition process, characterization of the resulting oxides using spectroscopic techniques, studies of the photoreduction of the oxides to lower oxidation states, and studies of the catalytic properties in oxidative and acid-catalyzed reactions.

Department of Chemistry

321. Morphological Aspects of Surface Reactions

White, J.M.

\$129,600

Comm. 512-471-3704

The long-range goal of this project is to establish correlations between the morphology of metals and their catalytic activity over a broad range of conditions. Silver and rhodium, individually and together, are of particular interest. Single crystals, thin films, and supported particles are all being used in surface chemical and model catalytic studies. Photon- and electron-stimulated, as well as thermal, chemistries are being developed. This experimental program continues to examine nonthermal methods for synthesizing catalytically interesting surface species whose thermal properties can be examined. For example, the electron-stimulated chemistry of benzene on Ag(111) shows evidence for the production of chemisorbed phenyl groups whose thermal and spectroscopic properties are under investigation. There is no ultraviolet (uv) photoactivity in this system. Studies are also being carried out on the surface reaction between potassium and gas phase methyl bromide. Even at 100 K, reaction occurs readily and ejects methyl radicals. Dissociative electron attachment to the incoming methyl bromide is proposed to account for this facile process.

Tulane University
New Orleans, LA 70118-5674

Department of Chemical Engineering

322. The Formation of Supported Bimetallic Clusters: The Effect of Support-Metal Precursor Interactions

Gonzalez, R.D.

\$70,000

Comm. 504-865-5772

The effect of support-metal precursor interactions on the structure and morphology of supported bimetallic clusters is being studied. Surface diffusion during reduction results in the agglomeration of Pt particles to form a supported catalyst which has a relatively low dispersion. When the decomposition of the Pt precursor is carried out in flowing oxygen, a Pt^{2+} precursor with low surface mobility is formed. This results in the formation of a more highly dispersed Pt catalyst. With Ru the results are the opposite; H_2 reduction results in high dispersion while oxygen pretreatment results in low dispersion. The surface composition and morphology of the resulting supported Pt-Ru bimetallic clusters made using these precursors is strongly dependent on the conditions under which the bimetallic particles are prepared. Treatment in oxygen at temperatures in excess of 300°C rapidly leads to phase separation. Silica supported Pd and Rh catalysts prepared using $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ and $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ as the metal precursor show that pretreatment in oxygen leads to the formation of poorly dispersed catalysts. Pretreatment in H_2 , on the other hand, leads to more highly dispersed catalysts. The chemistry of the oxygen and hydrogen treatment of the precursors is presently under study using *in situ* diffuse uv reflectance spectroscopy. The formation of mobile oxide species under oxygen flow is suspected. Preliminary indications suggest that these species are either oxides or superoxides.

University of Utah
Salt Lake City, UT 84112

Department of Chemistry

323. Ligand Intermediates in Metal-Catalyzed Reactions

Gladysz, J.A.

\$115,000

Comm. 801-581-4300

The project goal is the synthesis and study of homogeneous complexes containing ligand types ($-\text{CHO}$, $=\text{CHOH}$, $-\text{CH}_2\text{OH}$, C , $=\text{CH}_2$, $\text{H}_2\text{C}=\text{O}$, $-\text{OCHO}$, CO_2 , and so forth) intermediate in C_1/C_2 catalytic reactions. Mechanistic understanding of key steps and insight for the design of new catalysts is sought. Unusual processes involving monosubstituted alkene complexes have been discovered. The diastereomers (RS,SR)- and (RR,SS)- $[(\eta^5-\text{C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{CHR})]^+$ differ in the alkene enantioface bound to rhenium and equilibrate at 95°C in chlorobenzene (K_{eq} ca. 20). This seemingly necessitates alkene dissociation, rotation, and reattachment. However, equilibration is intramolecular (no exchange with deuterated alkenes), and occurs with retention of configuration at rhenium and without scrambling of $\text{C}=\text{C}$ deuterium labels. These and other data are best accommodated by

a mechanism involving an intermediate " σ bond complex." Also, many of these alkene complexes react with $t\text{-BuO}^- \text{K}^+$ to give vinyl complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}=\text{CHR})$. This constitutes a new type of C-H bond activation, a contrast to the allylic deprotonation mode commonly observed for cationic alkene complexes. Deuterium labeling shows that one geminal proton is stereospecifically abstracted. Fifteen aromatic aldehyde complexes of the formulae $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{O}=\text{CHAr})]^+$ have been prepared. A marked electronic effect on π/σ equilibria has been found. Electron withdrawing substituents (which enhance aldehyde π acidity and lower σ basicity) favor the π binding mode, while electron donating substituents have an opposite effect. The effects of temperature and solvent upon these equilibria have also been quantified.

324. Carbon-13 NMR of Solid-State Hydrocarbons and Related Substances

Grant, D.M.; Pugmire, R.J. **\$110,924**
Comm. 801-581-8854

The project objective is to develop new nuclear magnetic resonance (NMR) techniques to study solid organic materials. These techniques may be applied to gain structural and chemical information on model compounds and natural samples. The most important achievements have been (1) developing new spatial correlation techniques to measure ^{13}C chemical shielding tensors in single crystals; (2) improving theoretical methods for the calculation of shielding tensors; (3) developing the off-angle spinning technique to obtain principal values of shielding tensors; and (4) applying ^{13}C shielding tensor methods in the characterization of high-rank coals. The geometry of a mechanism that orients a single-crystal sample to characterize its chemical shift tensor was derived. This mechanism combined with two-dimensional correlation spectroscopy forms a powerful method for measuring chemical shift anisotropy in complex single crystals. Using two variable angle spinning techniques along with a variety of other NMR spectroscopic methods carbon-13 NMR shielding tensors have been determined for a variety of aromatic systems such as coronene, triphenylene, and several naphthalene derivatives. Theoretical calculations have been extended to these model compounds to explain and support the experimental conclusions. Spectroscopic analyses of nonprotonated to protonated aromatic carbons agree with elemental analyses and dipolar dephasing NMR techniques. These new methods are useful for analyzing the structure of high-rank coals; the fraction of condensed carbons obtained may be used to estimate average cluster size in condensed polyaromatic hydrocarbons, and these data are key parameters in coal devolatilization theories being developed in concert with personnel at the Sandia Combustion Research Facility in Livermore, California.

**Virginia Polytechnic Institute and State University
Blacksburg, VA 24061**

Department of Chemical Engineering

325. Influence of Surface Defects and Local Structure on Oxygenate Reaction Pathways over Metal Oxide Surfaces

Cox, D.F. **\$100,000**
Comm. 703-231-6829 **(20 months)**

The purpose of this project is to examine the effect of surface defects (primarily oxygen vacancies) and local structure on oxidation reactions over metal-oxide materials. The model system being investigated is the $\text{SnO}_2(110)$ surface because of the flexibility it allows in controlling surface cation coordination numbers, oxidation states, and the selective introduction of two different types of surface oxygen vacancies. These surface properties will be varied systematically, and their effect on surface reaction pathways will be investigated by thermal desorption spectroscopy (TDS) of C_1 to C_3 oxygenates (alcohols, aldehydes, and carboxylic acids). The role of crystallographically inequivalent forms of surface lattice oxygen will be investigated by preferential isotopic labeling of one of the two available forms of oxygen with ^{18}O . These studies will provide unique atomic-scale information about the relationship between local geometric structure and the selectivity and activity of oxygenate reaction pathways over a metal-oxide catalyst.

**University of Washington
Seattle, WA 98195**

Department of Chemistry

326. Model Cu-ZnO Catalysts for Methanol Synthesis: The Role of Surface Structure

Campbell, C.T. **\$95,000**
Comm. 206-543-3287

Copper/zinc oxide catalysts are highly active and selective for several reactions of importance in energy technologies: methanol synthesis, water-gas shift, and methanol steam reforming. These reactions are studied here using ultra-high vacuum surface science combined with reaction kinetics at high pressure (1 to 10^4 torr). These experiments apply surface analytical techniques to investigate the relationship between catalytic activity and the atomic-level surface structure of model catalysts based on Cu and ZnO single crystals. The structural and electronic properties of adsorbed intermediates are correlated with their kinetics in individual steps, which in turn are compared to the overall reaction rates. In this way, a detailed understanding of the active site involved in each step is developed. The kinetics of the forward and reverse water-gas shift reactions and many elementary steps have been measured on the clean and cesium-doped $\text{Cu}(110)$ surfaces. These results have clarified the reaction mechanism and the role of cesium promoters. The kinetics and thermodynamics of H_2 adsorption and formate hydrogenation on $\text{Cu}(110)$ have also been determined, leading to a fuller understanding of the mechanism of methanol synthesis. A simple method for testing the separate influences of gas

molecules' translational, rotational, and vibrational energy on surface reactions has been developed. Finally, the existence of a "magic angle" for detection in quantitative thermal desorption spectroscopy has been realized. These results should improve the fundamental understanding in Cu/ZnO catalysis and also in phenomena generic to catalysis such as surface interactions at metal/oxide support interfaces.

**Wayne State University
Detroit, MI 48202**

Department of Chemistry

**327. Reactive Characterization as a Probe of
the Nature of Catalytic Sites**

Brenner, A. **\$103,530**
Comm. 313-577-2503 **(24 months)**

This research is primarily concerned with achieving a better understanding of the nature of active sites on heterogeneous catalysts. A novel approach, termed reactive characterization is used. The patterns of activities and product distributions of catalysts are used to obtain information. Reactive characterization has provided a better understanding of the differences between homogeneous and heterogeneous catalysts and aided in the development of some novel catalysts. During the deuteration of ethylene, homogeneous catalysts and metal oxides usually give a high yield (>90%) of the trivial product, d₂-ethane, but metal surfaces yield considerable scrambled product so the yield of d₂-ethane is <50%. Strong mechanistic arguments can be made that the scrambling should only readily occur on catalysts that have sites which are both multiautomic and interacting (in the sense that a species can migrate from one site to another). It has been found that some conventional metal catalysts (Ni and Pd have been studied so far) can be poisoned so the yield of d₂-ethane exceeds 90%. This indicates that the poison does not merely lower the activity of the catalysts, but also causes the sites to become noninteracting so the surface now catalytically resembles a homogeneous catalyst. Thus, new catalysts have been made that have advantages (solid phase, chemical stability) of a heterogeneous catalyst but the improved selectivity of a homogeneous catalyst.

**University of Wisconsin at Madison
Madison, WI 53706**

Department of Chemical Engineering

**328. Experimental and Kinetic Modeling of
Acid/Base and Redox Reactions over Oxide Catalysts**

Dumesic, J.A. **\$105,000**
Comm. 608-262-1092

Studies have focused on the quantification of surface acidity for zeolites H-Y, H-Mordenite, and H-ZSM-5 and amorphous silica/alumina. Experimental techniques employed include microcalorimetry, solid-state nuclear magnetic resonance, infrared spectroscopy, and thermogravimetry. Microcalorimetric studies of pyridine

adsorption at 473 K show regions of site strength associated with Brønsted acidity, varying from 200 kJ/mol for H-Mordenite to 160 kJ/mol for H-Y and H-ZSM-5 to 140 kJ/mol for amorphous silica/alumina. Thermogravimetric measurements at 470 to 670 K were used to determine pyridine adsorption isotherms. In this complementary approach, the primary role of microcalorimetry is to measure heats of adsorption and to probe the acid strength distribution, and thermogravimetry is employed to determine entropies of adsorption and to quantify the number of acid sites with various strength. The entropy of pyridine adsorption on Brønsted acid sites was found to become more negative as the acid strength increased. On the strongest sites, pyridine is adsorbed in an immobile fashion, retaining its vibrational entropy and one degree of rotational entropy. Deuterium NMR has been utilized to probe the nature of the Brønsted acid sites and to study the interaction of these sites with pyridine and ammonia. Results indicate the presence of several types of Brønsted sites with different electric field gradients in the above zeolites.

Department of Chemistry

**329. Organometallic Chemistry of Bimetallic
Compounds**

Casey, C.P. **\$120,600**
Comm. 608-262-0584

The organometallic chemistry of bimetallic compounds is being investigated in an effort to discover new heterobimetallic compounds that can serve as catalysts for CO hydrogenation. The synthesis of heterobimetallic dihydrides in which one hydrogen atom is bonded to each metal is one target. The oxidative addition of a rhenium dihydride to platinum(O) complexes has provided a new route to heterobimetallic dihydrides. The kinetics and mechanism of the reaction of C₅H₅(CO)₂(H)RePt(H)(PPh₃)₂ with alkynes to produce rhenium-alkene complexes is being studied. The use of such compounds as catalysts for the hydrogenation of CO, alkenes, and alkynes is being investigated. Bimetallic compounds with one early and one late transition metal will be investigated since the resulting dihydrides are expected to have one hydridic and one acidic metal-hydrogen bond, and may act as powerful reducing agents for polar molecules such as CO. The synthesis and structure compounds with metal-metal double bonds is being studied. The addition of H₂ to metal-metal double bonds is being explored as a route to bimetallic dihydrides. The use of diphosphines with unusually wide bite angles (P-M-P, 110 to 150°) as ligands on hydroformylation and other catalysts is being studied in a search for more regioselective catalysts.

**University of Wisconsin at Milwaukee
Milwaukee, WI 53201**

Department of Chemistry

330. Aluminum Coordination and Active Catalytic Sites in Aluminas, Y Zeolites, and Pillared Clays

Fripiat, J.

Comm. 414-229-5852

\$165,889

(20 months)

This project aims to determine the aluminum coordination number in solids with large specific surface areas, that is, in selected transition aluminas, steamed Y zeolites, and new aluminum pillared silicas using primarily high-resolution solid-state ^{27}Al NMR, complemented with ^{29}Si NMR, in order to gain information on the nature of catalytic sites. Emphasis is on the effect of structural distortion of the Al coordination shells on the isotropic chemical shifts of ^{27}Al NMR resonances, the second order quadrupolar shift, and the quadrupolar coupling constant being studied by quadrupole nutation experiments. The local atomic arrangement near the aluminum nuclei being known, the nature of the surface acidity and, especially, the synergistic relations between Brönsted and Lewis sites would be studied by using adequate molecular probes. The ^{31}P MAS NMR chemical shift in $^{31}\text{P}(\text{CH}_3)_3$ and the infrared spectrum of chemisorbed pyridine would reveal the interaction with Brönsted or Lewis sites. The materials on which these studies will be performed will be carefully selected. The existence of pentacoordinated Al has been claimed in some transition aluminas, while strongly distorted tetrahedral- or penta-coordinated Al have been observed in steamed Y zeolites and in new pillared layered silicas. Two catalytic tests using the conversion of isobutane (for silico-aluminas, including zeolites) or of 1-butanol (for aluminas) will be carried out on the same samples in order to correlate catalytic activity with the nature of the acid sites.

**Yale University
New Haven, CT 06520**

Department of Applied Physics

331. Model Catalyst Studies of Active Sites and Metal-Support Interactions on Vanadia and Vanadia-Supported Catalysts

Henrich, V.

Comm. 203-432-4399

\$87,602

This project involves experimental investigations of the surface properties of model vanadia catalysts, the nature of active sites on those catalysts, and the interaction between catalyst metal atoms and oxide supports. Experimental techniques employed include ultraviolet and X-ray photoelectron spectroscopies (UPS and XPS), low-energy electron diffraction (LEED), high-resolution electron energy loss spectroscopy (HREELS), Auger spectroscopy, and inverse photoelectron spectroscopy; some of the work is performed at the National Synchrotron Light Source (NSLS). To study the electronic properties of vanadia surfaces, single-crystal V_2O_5 and V_2O_3 and the oxidation of V metal are used. The goal of this part of the work is to determine what types of sites are the active ones in real

vanadia catalysts. Model supported V catalysts are prepared by the deposition of V atoms onto single-crystal TiO_2 supports. Measurements on those samples are clarifying the complex interactions that take place between V, Ti, and O ions in titania-supported vanadia catalysts. Work at the NSLS involves resonant photoemission experiments on both stoichiometric and reduced TiO_2 (110) surfaces in order to obtain information about the hybridization of cation and anion electronic states on the surface. This research program is yielding valuable information about active sites on vanadia-based catalysts and on the interaction between vanadia and TiO_2 supports.

Department of Chemical Engineering

332. A Spectroscopic and Catalytic Investigation of Active Phase: Support Interactions

Haller, G.L.

Comm. 203-432-4378

\$103,500

This project involves the use of element specific spectroscopies, primarily NMR and X-ray absorption, to probe the local structure around catalyst components with the objective of correlating this local structure with activity and selectivity. One example of this approach using ^{29}Si NMR and Pt X-ray absorption, both of which involve an active phase interaction with an oxide support, will be described. Magic angle spinning ^{29}Si NMR has been demonstrated to measure the local partial charge on the Si. The acid strength of the Si-OH-Al bridging hydroxyl, as measured by 2-methyl-2-pentene (selectivity between double bond shift and methyl shift), correlates with the ^{29}Si chemical shift (partial charge). The Si partial charge (acid strength) of amorphous silica-alumina may be changed by changing either the tetrahedral units (T = Si or Al) bonded to the Si that composes the site or by changing the bond angles of the T-O-Si. Both change the partial charge on Si and can be measured by the ^{29}Si NMR chemical shift. The electronic and morphological structure of Pt particles interacting with L-zeolite have been probed by X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), respectively. Shifts in the threshold of the X-ray absorption edge of Pt are interpreted as the result of charge transfer from the zeolite support to the Pt particle (i.e., the zeolite host is behaving as a strong base). While it cannot be detected by X-ray absorption, exchange of the zeolite cation perturbs this Pt particle-zeolite interaction and alters the activity and selectivity of Pt catalyzed reactions of neopentane. While these interactions are particle size dependent, the effects of the zeolite cation exceed those of particle size alone and these appear to be rather long range.

Department of Chemistry

333. Alkane Photoreactions with Mercury Vapor

Crabtree, R.H.

Comm. 203-432-3925

\$108,460

The research is designed to understand alkane conversion and find new methods to synthesize derivatives suitable for large-scale application. Mercury photosensitized reactions with hydrogen to generate hydrogen atoms that undergo addition or subtraction reactions with alkanes or functionalized hydrocarbons is being investigated. Also

being examined are alkane conversions to alcohols, sulfonic acids, and ketones, as examples with academic and commercial significance. Hg^+ reacts with H_2 to give H atoms. These, in turn, react with a variety of organic compounds to give dehydromers. A large variety of functional groups are tolerated including amino, fluoroalkyl, epoxy, and carboxyalkyl. The products are formed in multigram quantities. The intermediate radicals can be trapped by any of a wide variety of traps to give functionalized derivatives (e.g., CO , SO_2 , and O_2).

334. Homolytic Activation of Hydrocarbons and Hydrogen by Persistent Metal Radicals

Heinekey, D.M. **\$100,000**
Comm. 203-432-3917 **(18 months)**

The thermal synthesis and isolation of rhenium(0) radicals of the general form $\text{Re}(\text{CO})_3(\text{PR}_3)_2$ (R = cyclohexyl, isopropyl, cyclopentyl) has been extended and generalized to the case of monocarbonyl complexes such as $\text{Re}(\text{CO})(\text{P}-\text{P})_2$ ($\text{P}-\text{P}$ = diphos and related ligands). The tetraphosphine complexes exhibit greater reactivity toward small molecules such as hydrogen than the previously studied bisphosphine complexes such as $\text{Re}(\text{CO})_3(\text{PCy}_3)_2$. These novel 17 electron species are very reactive toward a variety of small molecules including hydrogen and methane, to afford products of homolytic cleavage of $\text{H}-\text{H}$ and $\text{C}-\text{H}$ bonds. The mechanism of these reactions is under investigation. Preliminary results indicate that the reaction with hydrogen proceeds via a transient 19 electron hydrogen complex. Future work will include the synthesis of persistent biradicals through the use of spanning bidentate ligands and investigation of their structural and spectroscopic properties.

335. Energies of Organic Compounds

Wiberg, K.B. **\$73,585**
Comm. 203-432-5160

This research project is designed to provide information on energies and conformations of organic molecules via reaction calorimetry and theoretical calculations, and to use these data to improve empirical and semiempirical schemes for estimating the properties of organic compounds. Because of its importance in organic chemistry, a major effort is being made to understand the factors that control the structures, energies, and reactivity of carbonyl groups. The equilibrium constants for addition to carbonyl groups have been determined via measurements of equilibrium constants as a function of temperature. The results thus obtained are being checked wherever possible by direct calorimetric measurements. The conformations of the compounds formed by the addition to the carbonyl group are often determined by the anomeric effect, and it is being studied via calorimetric measurements and theoretical calculations. A method has been developed for measuring the heats of reduction of carbonyl groups, and it has been applied to a variety of carbonyl groups. An important application is to lactones, and it allows the determination of the strain energies and effects of conformation at the ester group. The hydration of cyclic alkenes is being studied in order to determine ring size effects on the energies of double bonds. Theoretical calculations and analysis of rotational barriers also continue.

Separations and Analysis

Auburn University Auburn, AL 36849-5128

Department of Chemical Engineering

336. Interfacial Chemistry in Solvent Extraction Systems

Neuman, R.D. **\$116,855**
Comm. 205-844-2017

Understanding the mechanisms of solvent extraction of metal ions in hydrometallurgical and nuclear waste processing technologies requires a comprehensive investigation of the interfacial behavior of extractant molecules. Present research emphasizes characterization of the macroscopic and microscopic interfaces that occur in acidic organophosphorus solvent extraction systems associated with Ni^{2+} , Co^{2+} , Zn^{2+} , and UO_2^{2+} . Recent advances in laser spectroscopic techniques provide novel tools to investigate interfacial extractant films. A pulsed Nd:YAG/dye laser system has been assembled to provide information about the dynamic properties and the structural organization of extractant molecules in the interfacial region. Optical reflectivity measurements on the liquid/liquid interface are being performed to determine the interfacial thickness of the solvent extraction systems. Fluorescence recovery after photobleaching (FRAP) studies will probe the nature of the microenvironment of the polar head groups of extractant films. The size and microstructure of the molecular aggregates in the bulk organic phase of solvent extraction systems are being investigated using small-angle neutron scattering (SANS) technique. Also, various spectroscopic techniques (FT-IR and NMR) are being employed to refine the reversed micellar model recently proposed by this group, for aggregation of metal-extractant complexes in acidic organophosphorus solvent extraction systems. This unique research program will significantly enhance the science and technology of solvent extraction processes.

Brigham Young University Provo, UT 84602

Department of Chemistry

337. Novel Macrocyclic Carriers for Proton-Coupled Liquid Membrane Transport

Lamb, J.D. **\$85,293**
Comm. 801-378-3841

The macrocycle-mediated metal cation transport in hydrophobic liquid membrane systems is being investigated. Potential macrocyclic carriers are synthesized, then screened by measuring pK_a values, extraction equilibrium constants, and partition coefficients for various metal cations. Macrocycles of particular interest are then studied in the potentially practical emulsion, hollow fiber, and dual module supported liquid membrane systems. A two-module hollow fiber system has been successfully implemented for use with less hydrophobic and proton-ionizable macrocycles. Research involves design,

synthesis, and characterization of new proton-ionizable macrocycles that permit coupling of cation transport to the reverse flux of protons. Macrocycles containing single and multiple pyridone, triazole, phosphono, and sulfonamide functional groups are under study where the ionizable proton is part of the macrocycle ring. Studies of these membrane systems also include modeling of both cation transport and membrane stability under various initial phase conditions.

Brown University
Providence, RI 02912

Department of Chemistry

- 338. Photochemical Generation of the Photoacoustic Effect**
Diebold, G.J. **\$94,000**
Comm. 401-863-3586

Basic research is being conducted on the properties of the photoacoustic effect. Part of the work is a continuation of past research on the time profile of photoacoustic waves generated by small bodies. In particular, the temporal waveforms generated by isotropic solid bodies irradiated by short pulse laser radiation will be investigated. A second facet of this work is the investigation of viscous effects on photoacoustic waveforms from small particles. This work is motivated by observations of deviations of the experimental waveforms from those predicted by theory. An important goal of the research is to investigate the response of particles to long pulse radiation. The theory predicts radically different behavior for the solutions in one and three dimensions. Solutions have also been obtained to the coupled equations for pressure and temperature that describe the production of acoustic waves by picosecond deposition of thermal energy by optical standing waves. The expressions obtained, which represent the first full solution to this problem, indicate that a frozen phase grating is obtained when the viscosity of the solvent is sufficiently high.

University of California, Los Angeles
Los Angeles, CA 90024

Department of Chemistry and Biochemistry

- 339. Multiheteromacrocycles that Complex Metal Ions**
Cram, D.J. **\$128,810**
Comm. 213-825-1562 **(24 months)**

The goals of this research are to design, synthesize, and test organic multiheteromacrocycles for their abilities to complex metal anions and large inorganic cations. The liganding systems are highly preorganized for binding during their syntheses rather than during their complexing acts. Bridged spherands for binding Li^+ and Na^+ are being examined. Ion specificity in binding of $\text{UO}_2(\text{CO}_3)_4^{4-}$ is a special goal that makes use of stereoelectronic complementarity between host and guest. Lipophilic hemicarcerands with large enforced cavities carrying positive charges in their interiors are being synthesized and examined. Correlations between host-guest

structures, binding free energies, rates of complexation-decomplexation, and solvation effects are being studied.

Columbia University
New York, NY 10027

Department of Chemistry

- 340. Utilization of Magnetic Effects as a Means of Isotope Enrichment**
Turro, N.J. **\$86,500**
Comm. 212-854-2175

The project objective is to provide a theoretical and experimental understanding of the factors leading to separation of isotopes based on their magnetic properties. The research performed has been driven by the radical pair theory which connects the reactivity of a geminate radical pair with magnetic interactions between the odd electrons and the nuclei. The optimization of these interactions requires that the radical fragments move in a restricted reaction space so that the separation of the fragments can occur and reduce important electron-electron interactions, yet return of the fragments into a zone of self reaction is possible. These ideas have led to investigations of radical pair chemistry in nanoscopic restricted reaction spaces (e.g., micelles, porous silica, zeolites, cyclodextrins) and has demonstrated the correspondence of the restricted space with the constraints imposed on a pair of radical centers by a connection of atoms as found in long chain biradicals. The efficient separation of ^{13}C (spin 1/2) from ^{12}C (spin 0) and ^{17}O (spin 5/2) from ^{16}O (spin 0) have been demonstrated. Current investigations are focused on the separation of "heavy" isotopes of atoms such as silicon and sulfur. In addition to the investigations of isotopic separations, the dynamics of the reactivity of the radical pair have been investigated by time resolved laser spectroscopy with analysis by optical and magnetic resonance methods.

University of Delaware
Newark, DE 19716

Department of Chemistry and Biochemistry

- 341. Linear and Nonlinear Spectroscopic Probing of Solute Interactions with Chemically Modified Silica Surface**
Wirth, M.J. **\$157,382**
Comm. 302-451-6771 **(24 months)**

Laser spectroscopic methods are used to investigate experimentally the structure and dynamics of monolayer stationary phases used in liquid chromatography. These studies address the molecular details of the chromatographic retention process to guide the design of more selective stationary phases. The spectroscopic experiments sense the configurations of the alkyl chains in bonded C_{18} stationary phases and the orientations of solutes interacting with these chains during chromatographic retention. Orientation and orientational distributions of chains and solutes are characterized by the polarization dependences of linear and nonlinear spectroscopic excitation. The dynamics of chains and solutes are characterized by their

picosecond reorientation behavior. These studies examine the effects of such important factors as chain density and mobile phase composition on the chain and solute orientations. These same experimental tools are being applied to the newly emerging liquid crystal stationary phases to understand the fundamental basis of liquid crystallinity at monolayer dimensions, as well as the principles of solvation by liquid crystal monolayers.

Duke University Durham, NC 27706

Department of Chemistry

342. *Studies of Multifrequency Phase-Resolved Fluorescence Spectroscopy for Spectral Fingerprinting*

McGown, L.B.

\$65,800

Comm. 919-684-3668

Exploration of dynamic spectral measurements for the classification, characterization, and fingerprinting of complex samples has branched into several promising new areas. Previous studies of the limits of resolution for simple, two-component systems helped to define those situations in which the addition of fluorescence lifetime selectivity becomes important as well as those cases for which lifetime selectivity fails. Novel data analysis strategies were developed for the three-way, excitation-emission-frequency arrays (EEFA) that are generated in frequency-domain, phase-resolved fluorescence lifetime techniques. The current focus is on real samples, including petroleum lubricants, coal-derived liquids, and human sera. Specific areas of activity include development of chemometric tools for characterization of these complex samples, studies of the effects of standard addition of individual components to the complex samples, explorations of organized bile salt media for solubilization and *in situ* isolation of fluorescence components, and the addition of chiral selectivity to the fluorescence lifetime data formats.

University of Florida Gainesville, FL 32611

Department of Chemistry

343. *The Glow Discharge as an Atomization and Ionization Source*

Harrison, W.

\$93,000

Comm. 904-392-0780

This research project focuses on fundamental and applied studies of the glow discharge as an analytical source for trace element analysis of solid samples by atomic emission, atomic absorption, and mass spectroscopies. Major emphasis will be on glow discharge mass spectrometry (GDMS) in current activity. Work is also conducted to improve understanding of the sputtering process. An rf discharge is being studied to develop methods for direct analysis of nonconducting materials without the need to mix these materials with conducting matrices, such as powdered copper. A comparison of rf and dc systems will be made with respect to sputter rates, ion yields, and

ratios of sputtered to discharge gas ions. Methods for pulsing the rf discharge are also under investigation. Another active project deals with pulsed dc glow discharges and the advantages obtainable in discriminating against molecular ions by time resolution. Setting a data gate in the trailing edge of the pulse causes the signal to consist of primarily ions from the sputtered sample material. A new project involves a dual discharge pulsed source in which one cathode is the sample and a second cathode is a reference standard. In this manner alternate pulsing of sample and standard permits direct comparison for elemental analysis, rather than resorting to the normal use of relative sensitivity factors. Interest continues in earth materials and the many analytical problems that the analyst encounters in attempting to obtain mass spectra, namely the many oxide contributions. By use of getter agents added to the sample, gas phase chemistry can be carried out in the plasma to reduce the magnitude of oxide signals. Differing degrees of success have been found with tantalum, rhenium, and titanium. Studies of electrothermal vaporization into a glow discharge are continuing, aiming for the ability to analyze solution samples of very small volumes.

344. *Development of Laser-Excited Atomic Fluorescence and Ionization Spectrometric Methods*

Winefordner, J.D.

\$89,300

Comm. 904-392-0556

Laser-excited atomic spectrometric methods are being investigated in order to achieve high spectral selectivity and detection power. The techniques being studied involve laser-enhanced ionization in flames, atmospheric furnaces, and low-pressure environments, laser-enhanced fluorescence in flames, inductively coupled plasmas (ICPs) and furnaces, and double resonance fluorescence in flames and ICPs for nonmetals. The techniques are used for both diagnostic measurements of spectral characteristics of atomic and ionic species in flames, plasmas, and furnaces as well as for analytical measurements. The emphasis is to achieve extremely high detection powers (subpart per trillion concentrations or femtogram amounts of elements) with extremely high spectral selectivities and very high freedom from matrix interferences. The diagnostic studies are directed toward (1) a more thorough understanding of the mechanisms of atomization, ionization, and dissociation of analyte species in plasmas and furnaces; (2) the optimization of experimental conditions to obtain the best analytical results by means of laser fluorescence dip spectroscopy; and (3) the development of resonance ionization detectors for ultrahigh photon detection sensitivity.

The George Washington University Washington, DC 20052

Department of Chemistry

345. *New High-Temperature Plasmas and Sample Introduction Systems for Analytical Atomic Emission and Mass Spectrometry*

Montaser, A.

\$69,361

Comm. 202-994-6480

New high-temperature plasmas, new sample introduction systems and diagnostic techniques, and a new plasma

source mass spectrometer are being developed for rapid elemental analysis of gases, solutions, and solids. These devices offer promise of solving singularly difficult analytical problems that either exist now or are likely to arise in the future in the various fields of energy generation, environmental pollution, biomedicine, and nutrition. Emphasis is on: (1) generation and fundamental investigation of helium inductively coupled plasmas (He ICP) that are suitable for the excitation of high-energy spectral lines, to enhance the detecting power of a number of elements; (2) development and characterization of low-cost sample introduction systems that consume microliter or microgram quantities of samples; (3) investigation of dual-beam, light-scattering interferometry for simultaneous measurements of droplet-size and velocity distributions of aerosols from various nebulizers, and for time-resolved studies of desolvated aerosol; (4) examination of utility of electrical mobility techniques for measuring particle size distribution in the range of 10 to 1000 nm; (5) simulation and computer modelings of He ICPs and mixed-gas discharges to predict the behavior of plasmas on a fundamental basis; and (6) development of a new ICP-mass spectrometer capable of sampling a variety of ICP discharges. Investigation addresses fundamental principles behind the measurements, evaluation of the analytical potentials of the devices developed, and demonstration of the analytical methods in representative samples.

**Georgia Institute of Technology
Atlanta, GA 30332**

Department of Chemistry

- 346. Fundamental Studies with a Monodisperse Aerosol-Based Liquid Chromatography/Mass Spectrometry Interface (MAGIC-LC/MS)**
Browner, R.F. **\$84,600**
Comm. 404-894-4020

Studies with the monodisperse aerosol-based interface have focused on ways of generating mass spectra from molecules which are sufficiently involatile or sufficiently thermally labile that normal processes for generating electron impact mass spectra cause extensive decomposition, with the loss of the molecular ion. Investigations with high-temperature surfaces of different materials have shown that by using very small particles (<50 nm), inert surfaces (such as gold), and relatively high temperatures (350°C) it is possible to obtain mass spectra from a number of different species types with a great improvement in the magnitude of the molecular ion peak. This is of particular interest, and has been extensively examined, for the cases of polynuclear aromatic compounds and phenyl urea pesticides. The coupling of supercritical fluid chromatography with the monodisperse aerosol interface, in place of reversed-phase liquid chromatography, has proved to be highly effective in allowing the production of electron impact mass spectra from exceptionally thermally unstable compounds, and has demonstrated the smallest ratio of thermal decomposition of certain test compounds (such as cholesterol) yet observed in any of the experiments.

**Hampton University
Hampton, VA 23668**

Department of Chemistry

- 347. Use of Ion Chromatography-DC Plasma Atomic Emission Spectroscopy for the Speciation of Trace Metals**
Urasa, I.T. **\$54,230**
Comm. 804-727-5398

This research involves trace metal speciation by using a combination of ion chromatography with dc plasma atomic emission spectrometry. Presently, focus is on the improvement of measurement sensitivity. New approaches, including postcolumn derivatization, are being explored to convert virtually 100% of the analyte in the chromatographic effluent into a form that can produce measurable analytical signals. The aim is to reduce the detection limits to below 1.0 ppb level. This research is also concerned with the elucidation of the solution chemistry of trace metals. The behavior of metal ions in different aqueous media can have a great influence on their speciation. The aim is to use the ion chromatography-dc plasma atomic emission spectrometry approach to study the changes that metal ions undergo as a result of changing solution properties.

**University of Houston
Houston, TX 77204-4792**

Department of Chemical Engineering

- 348. Mechanisms of Thickening, Cake Filtration, Centrifugation, Expression, and Ceramic Processing**
Tiller, F.M. **\$98,700**
Comm. 713-749-4316

Unification of the theory underlying solid/liquid separation operations is the principal objective of this research. Experimental confirmation of theoretical formulas and development of methodology for determination of empirical parameters appearing in the theory are a part of the program. Laws governing the relative flow of liquids and solids in suspensions and compacting particulate beds provide a common thread involving the various areas under investigation. Applications are made to the industrially important fluid/particle separation operations of sedimentation, thickening, cake filtration, centrifugation, expression, capillary suction, washing, and deliquoring. Specific areas of focus include waste minimization in environmental processes, slip casting of ceramics, capillary suction testing, optimization leading to maximizing production rates and minimizing the use of filter aids, mineral engineering, and formation damage in reservoirs. Among areas under investigation are particle movement in suspensions and sediments, centrifugal filtration and sedimentation, thickening, and development of testing procedures and correlations. Microscopic behavior of particle movement is being carried out using CATSCAN equipment. Macroscopic phenomena under scrutiny include the formation and compaction of cakes and sediments. The effect of flocculation and dispersion on the properties of suspensions and particulate beds is under study.

University of Idaho
Moscow, ID 83843**Department of Chemical Engineering****349. Drop Oscillation and Mass Transfer in Alternating Electric Fields**

Carleson, T.E.

\$37,468

Comm. 208-885-7652

Drop oscillations driven by an alternating electric field are efficient in enhancing direct-contact transport rates. The hydrodynamics of the electrically forced drop oscillations has been studied theoretically and experimentally as part of an effort to understand the effects of the electric field on the transport processes. Small amplitude oscillations of a charged conducting drop in an alternating electric field are studied using a first order perturbation model, which considers the primary effects of the net charge and the electric field as well as the secondary effects caused by charge redistribution on the deformed drop surface. The flow field is produced mainly by the primary effects. The contributions of the secondary effects influence resonant behavior. The predicted relation between the resonant frequency and the net charge asymptotically approaches Rayleigh's theory as viscosity and the field strength approach zero. As the electric forces increase, the resonant frequency decreases. The effects of the electric field and net charge have been investigated experimentally. The theoretical predictions agreed with the experimental measurements quantitatively. Enhancement of mass transfer rate will be estimated using the predicted flow field and measured experimentally by analyzing the drop phase composition.

University of Illinois at Urbana-Champaign
Urbana, IL 61801**Department of Chemistry****350. Thin Films Under Chemical Stress**

Bohn, P.W.

\$79,900

Comm. 217-333-0676

This project is aimed at the study of static and dynamic structure in organic thin films of nonuniform composition. Raman scattering and fluorescence excited by radiation injected into optical waveguide eigenmodes of the films are used to extract information about the temporal dependence of the active sites. A study of diffusive transport of aliphatic solvents in poly(styrene) was recently completed. It was confirmed that diffusion occurs by a case II mechanism, and thickness collapse was observed. This observation provided, for the first time in a micron-sized film, experimental evidence for the complete penetration of the solvent front through the film. This latter capability was possible because the waveguide experiment is not a mass-loading experiment. The understanding gained impacts directly on processes involving differential solubility in a macromolecular matrix (e.g., photoresist removal in lithography). In addition experiments have been initiated on permeation of water-soluble fluorescent tags through monolayers of amphiphilic molecules with and without the presence of an external perturbation. The goal in

these experiments is to develop a structure in which the permeability can be switched between high and low values via the imposition of an external signal. Reversible disordering of a zwitterionic amphiphilic layer with temperature and a large difference of permeability of poly(2-vinylpyridine) with and without the amphiphile was demonstrated.

351. Theta Pinch Discharges for Emission Spectrochemical Analysis

Scheeline, A.

\$69,800

Comm. 217-333-2999

A pulsed, magnetically constricted plasma (theta pinch) is being used for elemental chemical analysis. It has been shown in past years that any solid can be sufficiently vaporized and excited to reveal qualitatively the elemental composition of the solid. Efficiency of excitation has never been as great as one would desire, so modified discharge induction coils have been tested with the goal of increasing this efficiency. It has been demonstrated that excitation of solids increases at a somewhat greater than linear rate with peak discharge current. Simultaneously, an echelle spectrometer and charge-coupled array detector has been completed. This system will allow single-shot multielement analysis. Working curves for metallic elements in ceramic oxide powders have been obtained. Internal standardization is required for quantitative work. Typical precision without internal standardization is of the order of 20%, while with internal standardization, precision is of the order of 5% (using single emission lines of both standard and analyte). Stark and collisional broadening of lines are quite pronounced. While Mg(II) lines (for example) are expected to be self-reversed, evidence for such reversal is weak. The pinch has been shown to be useful for quantification of major and minor components in powdered refractory solids.

Kansas State University
Manhattan, KS 66506-3701**Department of Chemistry****352. Development of a Novel Hadamard Transform Infrared Spectrometer for Analytical Chemistry**

Fateley, W.G.

\$79,900

Comm. 913-532-6298

A Hadamard transform spectrometer (HTS) has been developed for the visible and near-infrared (NIR) spectral regions. A new generation of stationary Hadamard encoding masks has been developed for the no-moving-part near-infrared Hadamard transform (HT) Raman spectrometer. These new masks utilize polymer dispersed liquid crystal materials and avoid the use of NIR polarizers. Thus, NIR Raman spectra free from attenuation of strong polarized Raman bands caused by absorption by the NIR polarizers are now available. Demonstrations of spectral subtractions, the theoretical multiplex advantage, and a new selective multiplex technique have all been accomplished. A benefit of an HTS for quantitative chemical analysis is the ability to utilize data in the encodegram domain directly. This capability circumvents the requirement to transform the information into the spectral domain via the Hadamard transform. Resulting

calibrations using encodement data are equivalent to, or in some instances better than, those performed in the spectral domain. A Hadamard transform stationary interferometer has been constructed that is relatively simple to align, rugged, and since the interferogram is fixed in space, no sophisticated sampling mechanism is needed. This particular instrument can be made small and inexpensive and constitutes a no-moving-part spectrometer.

**Lehigh University
Bethlehem, PA 18015**

Department of Chemistry

353. Perforated Monolayers

Regen, S.L.

Comm. 215-758-4842

\$70,922

This research is aimed at creating a fundamentally new class of membranes, based on the construction of organized, two-dimensional assemblies of molecular pores. The immediate objectives of this work are to prepare first-generation perforated monolayer composite membranes and to define their permeation properties. The ultimate goal is to rationally design synthetic membranes, at the molecular level, which will provide an energy- and capital-efficient means of separating small molecules and ions on the basis of their size, shape, and polarity. Specific porous surfactants that are now being examined as building blocks for such assemblies are mercurated calix[n]arenes.

**Michigan State University
East Lansing, MI 48824-1322**

Department of Chemistry

354. Direct Probing of Chromatography

Columns by Laser-Induced Fluorescence

McGuffin, V.L.

Comm. 517-355-9715

\$80,000

A novel detection system has been developed that allows the direct examination of separation processes in chromatography. This system employs a single laser together with parallel detection optics and electronics to collect fluorescence emission at several points along an optically transparent capillary column. By measuring solute zone characteristics directly on the column, quantitative information concerning the separation process can be obtained as a function of spatial position. Any changes in solute zone characteristics, such as area, velocity, variance, asymmetry, and so forth, which occur between the detectors are the result of retention and dispersion processes in that region alone. Hence, this detection scheme effectively isolates the specific column regions of interest, affording a view of hydrodynamic and physicochemical processes not previously possible. This detection scheme has been employed to examine the influence of pressure on retention processes in reversed-phase liquid chromatography. A homologous series of linear, saturated fatty acids (C_{10} to C_{20}), labeled with the fluorescent probe 4-bromomethyl-7-methoxycoumarin, has been chosen as model solutes. When separated on an octadecylsilica stationary phase using methanol as the mobile phase, these ideal solutes

exhibit the theoretically expected logarithmic dependence of the partition coefficient on carbon number. As the inlet pressure is systematically increased from 1500 to 5000 psi, however, a substantial increase in the partition coefficient is observed. These results are interesting and surprising, since large increases in retention (10 to 25% for C_{10} to C_{20} , respectively) are observed for solutes that exhibit only dispersion (van der Waals) interaction forces. This increase in retention can be correlated theoretically to the local density of the mobile phase along the chromatographic column. Although presently limited to liquid chromatographic applications, these studies will be repeated for supercritical fluid chromatography where the mobile phase is highly compressible.

**University of Michigan
Ann Arbor, MI 48109-1055**

Department of Chemistry

355. Hadamard Transform Imaging

Morris, M.D.

Comm. 313-764-7360

\$94,000

Hadamard multiplexing is used to generate spatially and spectrally resolved Raman microscope images. Global illumination allows high incident laser power, and rapid (2 to 10 min typical) image acquisition time. The current design of a Hadamard Raman microscope employs a research microscope, single channel spectrograph, and CCD detection system. The multichannel CCD detector is used for simultaneous acquisition of up to 14 Raman images, thus allowing efficient examination of multicomponent materials and providing some background subtraction capability. Multispectral examination of the boundary region of polymer laminates and other composites is under way. Serial sectioning is used for three-dimensional Raman imaging. Nearest-neighbor deblurring has been implemented for reconstruction of three-dimensional imaging, and has been demonstrated to provide depth resolved images of organic crystals, polymers, and biological tissues. Development of iterative deconvolution techniques is under way, with the goal of providing three-dimensional Raman images with much higher signal/noise ratio than is presently available.

**University of Minnesota
Minneapolis, MN 55455**

Department of Chemical Engineering and Materials Science

356. Continuous Reaction Chromatography

Aris, R.; Carr, R.W.

Comm. 612-625-9568

\$79,900

The motivating principle behind this research is to employ chromatographic separations in continuous flow chemical reactors to accomplish separation of products at the same time that the reaction that is forming them takes place. The separation permits equilibria to be shifted, and the thermodynamic limitations of the reversible reaction in a fixed bed to be overcome. Thus high-purity product streams, and conversions far beyond the static equilibrium, can be obtained. A necessary condition for

continuous operation, in contrast with pulsed injection of feed, is that relative motion between the feedstream and the chromatographic bed must be achieved. One configuration meeting this criterion is the countercurrent moving bed. An experimental investigation has recently demonstrated that the predictions of high purity and high conversion that came out of previous theoretical studies are readily attained. The practical difficulties of moving a bed of granular solid against a gas stream have led to considerations of a situation in which countercurrency is simulated in a discontinuous manner by switching the feedstream along a series of entrances in a fixed bed. Switches are done at predetermined time intervals, and the feed is cycled back to the beginning after completing a pass along the fixed bed. An equilibrium stage model of this arrangement predicts excellent performance, and a differential model of a segmented section variant has been similarly successful. A laboratory-scale apparatus with computer-controlled switching has been constructed. The design is based upon the segmented section approach, as this presents fewer practical problems, and is guided by model calculations. Experimental testing is currently under way, with an investigation of the catalytic hydrogenation of 1,3,5-trimethylbenzene. Results to date corroborate the expectation of high product purity and high conversion. Since this reaction was also studied in the true countercurrent reactor, a comparison with simulated countercurrency is being undertaken. Exploratory investigations of the application of simulated countercurrency to reactions of more practical importance are also under way.

University of Missouri at Rolla Rolla, MO 65401

Department of Chemistry

357. *Use of Functionalized Surfactants and Cyclodextrins in Chemical Analysis*

Armstrong, D.W. **\$70,000**
Comm. 314-341-4429

(R)- and (S)-naphthylethylcarbamate- β -cyclodextrin bonded liquid chromatographic phases were originally developed for the normal phase separation of enantiomers. Although their selectivity resembled that of some of the earlier substituted cellulosic phases, the functionalized cyclodextrin stationary phases were much more stable as they were bonded to the silica support and not adsorbed. Because of their stability, the naphthylethylcarbamate- β -CD stationary phase was utilized in reversed phase separations. It was found that a completely different set of enantiomers was resolved by this column in the reversed phase mode. This included racemic pesticides such as Dyfonate, Ruelene, Ancymidol, and Coumachlor; as well as a variety of pharmacologically active compounds such as Tropicamide, Indapamide, Althiazide, Tolperisone, a sulfonamid from Merck Sharp & Dohme that has been resolved only by indirect methods, and over twenty others. It appears that the naphthylethylcarbamate- β -CD bonded phase is a highly effective, multimodal chiral stationary phase (CSP). A series of liquid cyclodextrin derivatives, 2,6-di-O-pentyl-3-O-trifluoroacetyl α -, β -, and γ -cyclodextrins (DP-TFA α -, β -, and γ -CD), have been used as highly selective chiral stationary phases for capillary gas chromatography. More than 150 pairs of

enantiomers were resolved; 120 on DP-TFA- γ -CD, which is the first reported γ -cyclodextrin stationary phase that is more widely useful than the β -cyclodextrin analogue. The enantiomers resolved include chiral alcohols, diols, polyols, amines, amino alcohols, halohydrocarbons, lactones, α -halocarboxylic acid esters, carbohydrates, epoxides, nicotine compounds, pyrans, furans, and so on. Identical α values were observed for diol, amine, and γ -halocarboxylic acid ester homologues, respectively. The relationship between the unusual selectivity behavior and separation mechanism is discussed.

National Institute of Standards and Technology, Gaithersburg Gaithersburg, MD 20899

Chemical Kinetics Division

358. *Competitive Ion Kinetics in Direct Mass Spectrometric Organic Speciation*

Sieck, L.W. **\$140,000**
Comm. 301-975-2563

This project involves the measurement of fundamental properties of gas phase ions. The NIST pulsed electron beam mass spectrometer is the prime experimental facility, and an FTICR instrument and triple MS system are also available. Emphasis is in two areas. One area is definition of the thermochemistry of association and cluster ions via variable-temperature equilibrium measurements. Correlation lines, which express the dependence of bond strengths upon the differences between the acidities or proton affinities of the two interacting partners, are then developed for predictive purposes for use in experimentally inaccessible systems. These investigations are augmented by collaborative efforts involving the study of intracluster ion-molecule chemistry occurring after ionization of neutral organic clusters produced in expansion beams. The second area involves extension and clarification of earlier kinetic studies from other laboratories to provide a more accurate database for gas phase ion and neutral thermochemistry. Currently, research includes extensive measurement of proton transfer equilibria as a function of temperature to provide interlocking thermochemical ladders which, when referenced to primary standards, provide absolute proton affinity and acidity scales. Related studies include ion pyrolysis and ion kinetics pertinent to plasma etching and electric breakdown in gaseous dielectrics.

University of North Carolina at Chapel Hill Chapel Hill, NC 27599-3290

Department of Chemistry

359. *Solid-State Voltammetry and Sensors in Gases and Other Nonionic Media*

Murray, R.W. **\$125,000**
Comm. 919-962-6296

Miniaturized electrochemical cells suitable for electrochemical voltammetry of electroactive materials dissolved

in or affixed to thin ionically conducting polymer films have been designed and tested. The cells are based on microdisk and microband electrodes and microlithographically fashioned microband electrodes. Experiments with these cells are aimed at developing a range of electrochemical methodologies, with appropriate boundary value theory, to bring the diagnostic power developed for electrochemical voltammetry in fluid electrolytes to rigid polymeric media experiments and to apply them to chemical problems of transport and electron transfer dynamics in rigid solvents. Secondly, the polymer solvent film can be exposed to a bathing gas whose constituents can interact in a plasticizing or in a chemically reactive way with the polymer solution, altering the observed electrochemical voltammetry. Such interactions presently form the basis for investigation of the molecular aspects of polymer plasticization effects and chemical reactivity in polymer phases, and may be applied to design sensors for bathing gas constituents.

**University of Oklahoma
Norman, OK 73019**

Department of Chemical Engineering and Materials Science

360. A Study of Micellar-Enhanced Ultrafiltration

Scamehorn, J.F.; Christian, S.D. **\$70,000**
Comm. 405-325-4382

Colloid-enhanced ultrafiltration methods are being developed to purify polluted wastewater or groundwater. In micellar-enhanced ultrafiltration (MEUF), surfactant is added to polluted water. The micelles (aggregates containing approximately 100 molecules) formed by the surfactants tend to solubilize the organics and bind the multivalent ions (e.g., heavy metals) if the surfactant is of opposite charge to these ions. In polyelectrolyte-enhanced ultrafiltration (PEUF), polyelectrolyte is added to the water and multivalent ions bind to the oppositely charged polyelectrolyte. In ion-expulsion ultrafiltration (IEUF), either surfactant micelles or polyelectrolyte of the same charge as the multivalent target ion is added to the water. The solution from each of these techniques is treated using ultrafiltration with membrane pore sizes small enough to block the passage of the colloid. In MEUF or PEUF, extremely pure permeate streams have been produced. In IEUF a permeate solution of high target ion concentration is produced and simultaneously separated from the colloid. Problems that have recently been addressed include the recovery of colloid from MEUF or PEUF for recycle to the process for economical operation, and the use of polymer/surfactant mixtures in MEUF for organic solute removal to reduce the concentration of surfactant in the permeate.

**Purdue University
West Lafayette, IN 47907**

Department of Chemistry

361. Reactions of Gaseous Metal Ions/Their Clusters in the Gas Phase Using Laser

Ionization: Fourier Transform Mass Spectrometry

Freiser, B.S. **\$98,700**
Comm. 317-494-5270

Work continues using laser desorption Fourier transform mass spectrometry (FTMS) to study the gas-phase chemistry and photochemistry of transition-metal-containing ions. A recent thrust has been to investigate the properties of a series of doubly charged species including Nb^{2+} , V^{2+} , Ta^{2+} , Zr^{2+} , and La^{2+} . Because early transition metals have relatively low second ionization potentials, their reactions with simple hydrocarbons yield interesting doubly charged products in addition to charge-transfer products. Studies on the ligated doubly charged ions are aimed at obtaining thermochemical information for comparison to their singly charged analogues. Surprisingly, the bond energy of M^{2+} to a particular ligand can be either greater or less than that of M^+ . An ongoing collaboration with Dr. Charles Bauschlicher at the NASA Ames Laboratory, has been particularly fruitful in providing theoretical insight into the nature of the stability and bonding of these interesting species. Techniques originally developed to measure ion kinetic energies in ion cyclotron resonance (ICR) spectrometry have been adapted to the FTMS to study the single charge-transfer reaction of M^{2+} with benzene. In this way detailed information about the partitioning of reaction exothermicity among the internal and translational modes can be obtained.

**Rensselaer Polytechnic Institute
Troy, NY 12180-3590**

Department of Chemical Engineering

362. Chemical Interactions Between Protein Molecules and Polymer Membrane Materials

Belfort, G. **\$140,000**
Comm. 518-276-6948 **(18 months)**

The objective of the research is to measure the intermolecular forces between interacting layers of proteins including bovine pancreas ribonuclease A, lysozyme, myoglobin, and human serum albumin, and ultrathin commercially relevant polymeric membranes. Polymers for these membranes include cellulose acetate, aromatic polyamide, polysulphone, and a copolymer mixture of polysulphone and poly(pyrrolidone) in order to obtain a series of varying polarity membranes. The Surface Force Apparatus is being used to obtain the intermolecular forces as a function of distance and solution conditions. The results of this study will provide a quantitative measure of the amplitude and extent of the interacting forces between proteins and polymeric membranes. This information is of interest in bioseparations, biocatalysis, biocompatibility, and biocolloid stability. With an understanding of these intermolecular forces, it should eventually be possible to choose membrane chemistries and operating conditions that minimize protein-membrane interactions and, hence, membrane fouling, a major cause of the decline in performance in membrane separation processes.

Department of Chemistry

363. Macrocyclic Ligands for Uranium Complexation

Potts, K.T.

\$98,000

Comm. 518-276-8460

A series of macrocyclic hosts for the uranyl ion has been designed using computer modeling techniques. These macrocycles contain six ligating oxygen atoms capable of binding in the equatorial plane of the uranyl ion arranged in a symmetrical manner in the macrocycle. Variables are introduced by inclusion of sulfur as a ligating atom, and by inclusion of peripheral subunits containing functional groups such as urea, biuret, thiobiuret, 1,3-diketone, and pyridine moieties. In the macrocycles prepared to date with alkane subunits in the periphery, it was not possible to control cavity diameters with sufficient accuracy (4.7 to 5.2 angstrom) to form uranyl complexes of adequate stability because of conformational flexibility in the macrocycle periphery. Syntheses of more highly preorganized macrocycles containing pyridine and other aromatic subunits, as well as functional groups influencing solubility in a positive manner, are now being completed. A new procedure for introducing a 4-vinyl substituent into the pyridine ring using triflate, Pd⁰, and vinyltributyltin chemistry has been developed to enable incorporation of these macrocycles into polymer systems.

State University of New York at Buffalo
Buffalo, NY 14214

Department of Chemistry

364. Determination of Solvation Kinetics in Supercritical Fluids

Bright, F.V.

\$54,741

Comm. 716-831-3615

The research centers on improving the understanding of solvation processes in pure and entrainer-modified supercritical fluids. Specific topics are (1) the kinetics for solvation in supercritical media; (2) the influence of entrainers on solvation; (3) the reversibility of the solvation process (i.e., can equilibrium information be recovered); (4) the effects of solvation on solute-solute interaction kinetics; and (5) the impact of fluid density on these processes. Because of its inherent sensitivity, selectivity, and time resolution, these processes will be investigated with multifrequency phase and modulation fluorescence spectroscopy. The results from this project should provide insight into the kinetics and mechanisms of solute-fluid, solute-entrainer, and solute-solute interactions in supercritical media. In turn, this information can lead to a more accurate molecular understanding of supercritical fluid solvation.

Syracuse University
Syracuse, NY 13244

Department of Chemical Engineering and Materials Science

365. Mechanisms of Gas Permeation through Polymer Membranes

Stern, S.A.

\$84,600

Comm. 315-443-4469

A new relation was derived recently to express the dependence of gas solubility in glassy polymers on pressure, under conditions where the polymers are significantly plasticized by the penetrant gases. This relation is based on the use of a modified Williams-Landel-Ferry equation and shows that, for such conditions, the gas solubility isotherms have an inflection point which indicates a change in the solution mechanism. At pressures below the inflection point the solubility isotherms exhibit the concavity characteristic of the dual-mode sorption behavior observed in many glassy polymers. At higher pressures, by contrast, the solubility isotherms become linear, as observed for gases in rubbery polymers in the Henry's law limit. This change in solution mechanism occurs when the polymer is plasticized to such an extent that the glass-transition temperature of the gas/polymer system is depressed to the temperature of the solubility isotherm. The new relation has been successfully tested with solubility data for a variety of gas/polymer systems reported in the literature, and will also be tested experimentally with other systems. This theoretical approach is being extended to describe the transport of plasticizing gases in glassy polymers (by diffusion) and through polymer membranes (by permeation).

366. Particle Deposition in Granular Media

Tien, C.

\$94,000

Comm. 315-443-4050

This study is concerned with the analysis and investigation of the effect of deposition on aerosol filtration in granular media. The specific topics to be investigated include: (1) experimental determination of collection efficiencies of polydispersed aerosols, (2) computer simulation of deposition of polydispersed aerosols, and (3) development of a new image-analysis technique for examining the change of granular media structure caused by aerosol deposition and formulation of a network model for representing clogged granular media.

University of Tennessee
Knoxville, TN 37996-1600

Department of Chemistry

367. Polymer-Based Separations: Synthesis and Application of Polymers for Ionic and Molecular Recognition

Alexandratos, S.D.

\$85,450

Comm. 615-974-3399

Research focuses on the synthesis of polymer-supported reagents which can be used to study polymer/ion and polymer/molecule interactions. The aim of the research is to

design polymeric reagents with an optimized performance in ionic and molecular separations from multi-component solutions. A three-part series has recently been published which helps define the mechanisms of polymer-based separations for metal ions. Different polymeric reagents were contacted with a series of metal ions at varying initial concentrations in solutions of different pH and ionic strength. It was found that the inherent polymer/ion affinity is best defined in dilute solutions ($10^{-5}N$) at acid concentrations which lead to a ratio of solution H^+ to polymer ligand of 1:1 or less. The relative coordinative affinity for M^{n+}/H^+ displayed by the ligand is best defined in dilute solutions and high acid concentrations ($\geq 2N$ nitric acid). The sensitivity of the polymer to loading effects may then be defined by increasing the initial metal concentration from $10^{-5}N$ to $10^{-1}N$. A novel coordinating resin was found to have excellent gold sorption properties from alkaline solutions; it was recently granted a U.S. patent. Polymer-molecule interactions are also being studied with the current emphasis being on the effect of the polymer support on the extent to which the ligand interacts with a target molecule.

368. Study of the Surface Properties of Ceramic Materials by Chromatography
Guiochon, G. **\$81,600**
Comm. 615-974-0733

The aim of this work is the better understanding of the surface properties of solid powders, in view of characterizing the powder lot and predicting some of the properties of the material obtained after processing. This work is relevant to the production of advanced ceramic materials and could provide new methods for the quality control of the powders used to make green bodies. A correlation between the parameters measured and the quality of a number of lots of alumina powders has been established. The procedure developed involves the determination of the distribution of adsorption energy on a surface for a series of selected probes. This determination is made by measuring the adsorption isotherm of the probe and solving the integral equation which relates the adsorption energy distribution, the adsorption isotherm on each type of sites (assumed to be homogeneous), and the measured isotherm. The experimental isotherm is easily obtained by frontal analysis. Programs permitting the calculation have been developed and systematic determination on various samples of alumina and silica have been conducted. The adsorption energy distribution of a surface depends much on the nature of the probe used. Several probes are needed to characterize a surface.

369. Capillary Liquid Chromatography Using Laser-Based and Mass Spectrometric Detection
Sepaniak, M.J. **\$74,000**
Comm. 615-974-8023

The focus of this research is the practical development of capillary electrokinetic separation techniques for the analyses of volume-limited, complex samples, and difficult-to-resolve mixtures. Work has continued with characterization and utilization of micellar electrokinetic capillary chromatography (MECC). With this technique, neutral compounds are separated based on differential partitioning between electrokinetically migrating aqueous and micellar components in the mobile phase. In addition,

the use of capillary zone electrophoresis (CZE) for separations of charged solutes has been investigated. There are five research projects currently in progress. The first project involves investigating factors that influence efficiency and detectability of separated proteins. Laser-based natural protein fluorescence and precolumn and on-column fluorescence derivatization have unique advantages and disadvantages in the detection of proteins/peptides. In the second project, metal ions present in real matrices have been separated and detected with low limits of detection (LODs) using mobile phases that incorporate fluorescing chelates. The manipulation of metal migration velocity via adjustments of running buffer composition was demonstrated. Current efforts are focused on separations of rare earths by this method using time-resolved and multidimensional laser fluorometric detection. In the third project, using retention and flow rate parameters obtained from isocratic separations, computer simulated elution profiles have been generated to determine optimum gradient elution conditions for separating standard mixtures. Refinements in the gradient instrumentation are in progress. Chiral-ordered surfactants (bile salts) have facilitated the MECC separations of certain enantiomeric and moderately hydrophobic compounds in the fourth project. The separation of isomeric polycyclic aromatic hydrocarbon (PAH) compounds is under study. Lastly, preliminary investigations into the use of affinity reagents (e.g., antibodies) as mobile phase additives to provide highly selective electrokinetic-based affinity separations are being conducted.

Texas A & M University
College Station, TX 77843-3255

Department of Chemistry

370. Development of Laser-Ion Beam Photodissociation Methods
Russell, D.H. **\$78,960**
Comm. 409-845-3345

This project emphasizes laser-ion beam photodissociation methods for probing the dynamics of dissociation reactions of highly activated ionic systems. The experimental hardware and methods are developed, and studies on the photochemistry and photophysics of ionized peptides and transition metal clusters are in progress. In addition, the potential analytical utility of laser-ion beam photodissociation for the structural characterization of large biomolecules is being evaluated. A second-generation photodissociation apparatus is now completed and used routinely for a range of tandem mass spectrometry research. The instrument consists of a high-resolution magnetic sector instrument (Kratos MS-50) as MS-I and a high-sensitivity/high-resolution reflectron time-of-flight instrument as MS-II. Photodissociation on this instrument is performed by using a high-power, pulsed excimer laser. The primary objective of the current research is to improve the sensitivity of MS-MS experiments by 100 times (10 to 100 femtomole) and the mass resolution of MS-II by 5 to 10 times (1000 to 10,000). The focus of the current work is on structural characterization of peptides and organo-alkali metal ions of peptides and nucleotides. This instrument is also used for performing matrix-assisted-uv-laser desorption ionization of polar, thermally labile biomolecules.

Texas Tech University
Lubbock, TX 79409-1061

Department of Chemistry and Biochemistry

371. Metal Ion Complexation by Ionizable Crown Ethers

Bartsch, R.A.
Comm. 806-742-3069

\$89,300

Goals of this research are the synthesis of new metal ion complexing agents and their applications in metal ion separation processes. New crown ether carboxylic acids, phosphonic acid monoethyl esters, phosphonic acids, and sulfonic acids are being synthesized and tested to probe the influence of structural variation within the ligand on metal ion complexation behavior. These novel compounds are being tested in solvent extraction and in bulk, emulsion, and polymer-supported liquid membrane transport of alkali metal and alkaline earth cations. Novel ion exchange resins are being prepared from ionizable crown ethers. In addition to ion exchange sites, these resins also possess crown ether units. Sorption behavior of these resins for alkali metal and alkaline earth cations and their application in concentrator columns for these metal ions are being explored.

372. Novel Approaches to Ionic Chromatography

Dasgupta, P.K.
Comm. 806-742-3064

\$75,200

The project objectives are (1) to achieve high-sensitivity, high-resolution chromatographic techniques for the analysis of ionic species and (2) to explore new strategies for the identification of ions and the reduction of consumables. Novel uses of the ion exchange process and properties of ion exchangers are explored. Recent accomplishments include the following work. (1) The development of a rapid and precise technique for the conductometric measurement of the disassociation constant of a weak acid. The determination does not require the measurement of pH and can be made in minutes. (2) An amperometric micro sensor for water vapor based on electrolytic current conduction in a perfluorosulfonate ionomer thin film either by itself or as a composite with P₂O₅ has been developed. The sensor can measure water from 2 ppm to saturation levels. (3) Several types of membrane-based generators that can electrodiagnostically generate ultrapure ionomer NaOH solutions have been developed. These solutions have been used for gradient ion chromatography to obtain unprecedented baseline stability, calibration stability, and response linearity. The eluent concentration gradient is controlled by electrical programming of the source rather than by mechanical proportioning of two or more liquids. The generation procedure can be applicable to most electrochemically stable ionic chemicals which can be produced in solution in ultrapure form.

University of Texas at Austin
Austin, TX 78712-1062

Department of Chemical Engineering

373. Synthesis and Analysis of Novel Polymers with Potential for Providing Both High Permselectivity and Permeability in Gas Separation Applications

Koros, W.; Paul, D.
Comm. 512-471-5866

\$85,102

This project focuses on synthesis and characterization of polymeric materials for advanced gas separation membrane applications. The fundamental sorption and diffusion coefficients governing the permeability and permselectivity of such materials are being measured with both pure and mixed gas feeds. Polymers in the polycarbonate, polyester, and polysulfone families with high permeabilities for important commercial gases such as hydrogen, carbon dioxide, and oxygen have been identified by systematic variation in the structures. In addition to high permeabilities, several of these materials have shown very attractive permselectivities for gas pairs such as H₂/CH₄, CO₂/CH₄, and O₂/N₂. Applications at elevated temperatures are receiving extra attention. Structural changes that produce favorable trade-offs in the permeability and selectivity within a given family have in common a tendency to produce simultaneous inhibition of intrachain mobility and interchain packing. This rule, while qualitative, has been invaluable for identifying structures with potential as advanced membrane materials. A fortunate coincidence appears to exist in the fact that the molecularly rigid materials being developed also have better thermal stabilities than more flexible chain analogs in the same polymer families. The testing includes studies up to 1000 psia, so realistic conditions like those encountered in actual field conditions can be simulated. The high pressure range of the studies allows ranking the materials not only according to their intrinsic properties, but also according to their ability to resist plasticization-induced softening and selectivity loss.

University of Utah
Salt Lake City, UT 84112

Department of Chemistry

374. Pulsed Laser Kinetic Studies of Liquids under High Pressures

Eyring, E.M.
Comm. 801-581-8658

\$77,000

The volume reaction coordinate profile can be obtained for processes in liquids by measuring rates with the liquid under high pressures. Knowledge of the volume profile permits deduction of the reaction mechanism. A high-pressure sample cell for pulsed laser excitation of the sample liquid and conductimetric reaction rate measurement is being used to study the laser-induced dissociation of pure liquid water into hydronium and hydroxide ions. Concurrently, pulsed laser flash photolysis of M(CO)₆ [M≡Cr, Mo, W] in the presence of bidentate ligands L such as 1,10-phenanthroline is being carried out under high pressures. The coordinatively unsaturated species

$M(CO)_5L$ produced by photolysis undergoes thermal chelation by elimination of CO to yield $M(CO)_4L$. Resulting volumes of activation are useful indicators of reaction mechanism. A third concurrent study involves long-range electron transfer in proteins modeled by Marcus theory in which the parameter, λ , is the reorganization energy. The λ represents a barrier to electron transfer and includes effects of ligation and solvation of the metal center. A system permitting elucidation of λ is a uroporphyrin/cytochrome c self-association complex in aqueous solution. Laser photoexcitation of the porphyrin metal center induces electron transfer, leading to pressure-dependent rates for long-range electron transfer and resulting new information about λ .

Department of Metallurgy and Metallurgical Engineering

375. *Hydrophobic Character of Nonsulfide Mineral Surfaces as Influenced by Double Bond Reactions of Adsorbed Unsaturated Collector Species*

Miller, J.D. **\$94,000**
Comm. 801-581-5160

In situ Fourier transform infrared (FTIR) spectroscopy has been used to monitor in real time the adsorption of surfactants common to the froth flotation process. Using mineral crystals machined into internal reflection elements (IREs), in what are termed "reactive IREs," the adsorption of surfactants at dilute equilibrium concentrations has been monitored in real time by internal reflection spectroscopy (IRS). Mineral/surfactant systems studied by this method include fluorite (CaF_2)/sodium oleate, sylvite (KCl)/octylamine hydrochloride, and sapphire (Al_2O_3)/sodium dodecyl sulfate. This novel approach to the study of adsorption processes has allowed determination of the surfactant orientation, bonding characteristics at the surface, and adsorption density. Research has focused primarily on the fluorite/sodium oleate system. Specifically, it has been shown that the first monolayer of chemisorbed oleate has a distinctly different infrared spectrum than subsequent precipitated layers of calcium oleate. Also, complete adsorption isotherms for oleate on a reactive fluorite IRE have been determined at various temperatures. These isotherms were constructed from spectra in both the mid-infrared and the near-infrared region of the electromagnetic spectrum. In addition, most recently, conformational changes in the hydrocarbon chain of the adsorbed surfactant have been detected. These thermotropic transitions at the surface of mineral crystals clearly show when the adsorbed surfactant is in a micelle-like state or in a more condensed state by spectral changes corresponding to the number of gauche bonds in the hydrocarbon chain. Future research should establish how these conformational changes at the interface influence the hydrophobicity of a particular system. Finally, the oxidation/polymerization reaction of adsorbed oleate monomers, found in previous transmission work, is being studied *in situ* by this innovative FTIR/IRS technique. This oxidation/polymerization phenomenon is being investigated as a function of system variables (oxygen concentration, temperature, and applied electrochemical potential).

Virginia Commonwealth University Richmond, VA 23284-2006

Department of Chemistry

376. *Compensation for Peak Shifts and Variable Background Responses in Fluorescence Spectroscopy*

Rutan, S.C. **\$77,401**
Comm. 804-367-1298

The fluorescence responses observed for polyaromatic hydrocarbon compounds are susceptible to changes in the chemical surroundings of the molecules. Perturbations to the spectral responses arising from the presence of variable background components or solvent-dependent spectral shifts cause errors in algorithms developed for the identification and quantification of fluorescent species. The purpose of these studies is the development of mathematical methods that allow determination of fluorescent species, despite errors caused by these perturbations to the spectra. Current work is focused in two areas. The first area is the development of an on-line fluorescence spectroscopic detector for high performance liquid chromatography, based on an intensified diode array. Windows programs that allow for control of the liquid chromatography gradient conditions, which can be run concurrently with the diode array manufacturer's software, have been developed. This allows collection of fluorescence spectra "on-the-fly" from liquid chromatographic eluants. Data analysis algorithms can then be implemented which can correct for sample dependent background responses and solvent dependent response shifts. These methods allow fluorescence spectral detection to be used reliably in the detection of polyaromatic hydrocarbon compounds separated using both isocratic and gradient elution. Quantification of amino anthracene isomers which show a high degree of both chromatographic and spectroscopic overlap, has been achieved.

University of Wyoming Laramie, WY 82071

Department of Chemistry

377. *Solid-Surface Luminescence Analysis* Hurtubise, R.J. **\$93,670** Comm. 307-766-6241

The objective of this project is to acquire a basic understanding of the physical and chemical interactions that are responsible for the room-temperature fluorescence and room-temperature phosphorescence of organic compounds adsorbed on solid matrices. Several spectral techniques are used to study the interactions. Filter paper, sodium acetate, and cyclodextrin/salt mixtures are being used as solid matrices for the adsorbed compounds. Experiments are being performed in which the temperature and humidity are varied for model compounds adsorbed on solid matrices. Also, experiments are performed to determine the modulus of filter paper as a function of temperature. From the luminescence data acquired, quantum yields, photophysical rate constants, and rotational relaxation times of adsorbed species are calculated. The calculated parameters of the adsorbed compounds and properties of

the solid matrices are correlated to develop interaction models. For example, a recent theory on the modulus of paper relates the modulus of paper to the number of effective hydrogen bonds in paper. By using this theory and the solid-matrix luminescence data of model compounds, it is possible to derive equations that directly relate the modulus of filter paper to phosphorescence lifetimes of model compounds adsorbed on filter paper.

Heavy Element Chemistry

Florida State University
Tallahassee, FL 32306

Department of Chemistry

378. Research in Actinide Chemistry
Choppin, G.R. \$111,000
Comm. 904-644-3875

This research emphasizes the basic studies of the behavior in solution of the actinide elements and of the chemically related lanthanide elements. The systems are chosen for investigation because the data can provide increased understanding of the principles governing their chemical behavior. The data may also be of direct value for modeling calculations of the behavior of actinides in environmental and waste repository systems or in improved separation schemes of these elements. Emphasis continues on the thermodynamic, kinetic, and spectroscopic (absorption and luminescence) studies of the complexation and redox reaction of the actinides. Binding of actinides in the III through VI oxidation states to humic acid is very rapid, but originally most of the An is "weakly" bound and two days were found to be required to reach equilibrium between "strong" and "weak" binding. Binding studies of NpO_2^+ in humic acid solutions gave stability constants which had no dependence on pH in contrast to the behavior of the complexation of An(III), (IV), and (VI). Other systems under study at present involve actinide interaction with silicate ligands. The fluorescent half-life method has provided information on the residual hydration in these complexes and in a number of systems used in solvent extraction separations of actinides.

University of New Mexico
Albuquerque, NM 87131

Department of Chemistry

379. Development of Immobilized Ligands for Actinide Separations
Paine, R.T. \$192,000
Comm. 505-277-1661 (24 months)

The primary goals of this project are (1) to establish fundamental data for the design of new families of organic extractants suited for the separation of f-element ions from complex matrices and (2) to develop methods for preparing separation agents covalently attached to solid supports. In particular, synthetic schemes are devised that provide ligands containing two or more functional

groups typically in 1,2 positions on a carbon backbone, with high orientational flexibility. Functional groups most commonly employed are organo-phosphoryl, nitrosyl, sulfinyl, sulfonyl, and carbonyl. The coordination chemistry of new ligand types is studied and systematized in an effort to determine key factors that result in selective f-element binding. The extraction properties of selected ligands are also characterized by radio-chemical methods. Ligands that demonstrate favorable separation properties are further functionalized in order to attach the ligand fragment to a solid organic or inorganic support. Steric and electronic factors that subsequently influence the separation properties of immobilized ligands are examined.

Ohio State University
Columbus, OH 43210

Department of Chemistry

380. Molecular Orbital Studies of the Bonding in Heavy-Element Organometallics
Bursten, B.E. \$62,000
Comm. 614-292-1866

The ongoing investigation into the bonding in cyclopentadienyl actinide organometallics Cp_3An ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; An = Th through Cf) via quasi-relativistic X_α -SW molecular orbital calculations has led to a new understanding of the changes in An-Cp bonding as a function of actinide element. These studies have also suggested new ventures in the organometallic chemistry of zirconium, which should parallel that of thorium to a certain extent. The application of more sophisticated electronic structure methods to large actinide systems has been successfully achieved during this period as well. Fully-relativistic DV- X_α calculations have been carried out for a series of trivalent uranium and plutonium complexes, such as $\text{An}(\text{CH}_3)_3$, $\text{An}(\text{NH}_2)_3$, and Cp_3An (An = U, Pu). These studies provide a much clearer picture of the interplay between ligand-field and spin-orbit effects on the electronic structures of the complexes. *Ab initio* calculations with relativistic effective core potentials have been carried out for the diatomic molecule U_2 . These studies show conclusively that relativistic effects will be key in determining molecular architectures that could support direct actinide-to-actinide bonds.

SRI International
Menlo Park, CA 94025

Physical Sciences Division

381. Chemistry of Gaseous Lower-Valent Actinide Halides
Hildenbrand, D.L.; Lau, K.H. \$70,000
Comm. 415-859-3436

The project objective is to provide accurate thermochemical information for key actinide halide, oxyhalide, and related systems, starting with the uranium and thorium halides, so that the basic factors underlying the energetic and structural aspects of the chemical bonding in these systems can be elucidated in a systematic way. The principal focus is on the gaseous lower-valent halides, since

there is little thermodynamic or spectroscopic information on these species. Bond dissociation energy and absolute entropy data are derived from chemical equilibrium measurements made primarily by high-temperature mass spectrometry. Current studies are concerned with the gaseous tetrabromides and tetraiodides of uranium and thorium, the neptunium fluorides and oxyfluorides, and the oxychlorides of uranium and thorium. Sublimation entropies indicate that the gaseous uranium tetrahalides and some thorium tetrahalides most likely have distorted tetrahedral structures, while other thorium tetrahalides are regular tetrahedra. Bond energy patterns also show significant differences in the two series. Clarification of these trends will be useful in modeling the thermochemistry of the heavier actinides, which will be much more difficult to study experimentally.

**University of Tennessee
Knoxville, TN 37996-1600**

Department of Chemistry

382. Physical-Chemical Studies of Transuranium Elements
Peterson, J.R. **\$153,000**
Comm. 615-974-3434

This project provides training for pre- and postdoctoral students in chemical research with the transuranium elements. The goals of this project are to interpret and correlate the results of continuing investigations of the basic chemical and physical properties of these elements. New knowledge is being accumulated in the following areas: (1) the role of the 5f electrons in the bonding in actinide elements and compounds; (2) the extent and magnitude of the actinide contraction; (3) the spectroscopic, crystallographic, thermodynamic, and magnetic properties of these materials as related to general theories; (4) the chemical and physical consequences of radioactive decay in the bulk-phase solid state; and (5) the range of validity of the actinide hypothesis. Current research emphasis is on: (1) characterization of lanthanide and actinide compounds via phonon Raman spectroscopy; (2) use of fluorescence spectroscopy to probe the structure of lanthanide and actinide compounds; (3) X-ray diffraction of actinide materials under pressure; (4) absorption, luminescence, and Raman spectrophotometry of lanthanide and actinide materials under pressure; (5) measurement of the enthalpies of solution of selected lanthanide and actinide compounds; (6) direct or indirect (via radioactive decay) synthesis of actinide compounds containing unusual oxidation states; (7) broader applications of studies to determine the physical and chemical consequences of radioactive decay in the bulk-phase solid state; and (8) growing single crystals of actinide elements and compounds on the milligram scale.

Chemical Engineering Sciences

**University of California, San Diego
La Jolla, CA 92093**

Department of Applied Mechanics and Engineering Sciences

383. Premixed Turbulent Combustion
Libby, P.A. **\$56,400**
Comm. 619-534-3168

This project involves several areas of research concerned with premixed turbulent combustion. The first relates to the characteristics of laminar flamelets as they arise in turbulent flames. A study of such flamelets in counterflowing streams subject to swirl is presently under way. The analysis for low rates of swirl has been completed. Beyond a critical rate of rotation, multiple stagnation planes appear and the situation calls for an entirely different asymptotic analysis which has been completed. The second area of research concerns counterflowing premixed turbulent flames. These flames are under experimental investigation at several institutions and are becoming recognized as providing a convenient vehicle for the study of a variety of phenomena connected with such flames. The portion of this work dealing with extinction is being combined with experiments carried out at Cambridge. The formulation for a third approach based on the Bray-Moss-Libby model, presumably the most realistic, is being reassessed because preliminary numerical results suggested that the modeling used to close the equations was seriously flawed. The numerical analysis of highly idealized premixed flames in a duct is progressing.

**Clarkson University
Potsdam, NY 13699-5705**

Department of Chemical Engineering

384. Analysis and Computer Tools for Separation Processes Involving Nonideal Mixtures
Lucia, A. **\$50,000**
Comm. 315-268-6674

The analysis framework for multistage separation processes has been expanded to include both composition specifications for binary separators and heat duty and pressure profile specifications for multicomponent separators involving homogeneous mixtures. In each case, solution uniqueness has been established. Also, results for multicomponent, multistage separators with fixed temperature and pressure profiles have been refined to more accurately estimate the domain on which any solution, which is unique, is defined. Past analysis has been used to develop a new bubblepoint algorithm capable of handling both wide boiling and narrow boiling mixtures. This new bubblepoint method has been tested on several literature examples and shown to perform well. Periodic and chaotic behavior of Newton's method on separation problems in which all fluid phases are modeled by an equation of state

have been studied. The geometric structure of the Julia set associated with a typical chaotic attractor has been illustrated, and it has been shown that the fine-scale geometry of periodic behavior in parameter space is given by the Mandelbrot set. An extension of Powell's dogleg strategy to the complex plane has been developed and global convergence to a root has been illustrated for a wide variety of initial values.

Colorado State University Fort Collins, CO 80523

Department of Chemical Engineering

385. *Study of Improved Methods for Predicting Chemical Equilibria*

Lenz, T.G.; Vaughan, J.D. **\$95,642**
Comm. 303-491-7871

The equilibrium composition of chemically reactive systems can be determined experimentally, but considering the extremely large number of potentially valuable reactions, relying solely on measurements would be prohibitively expensive. This project involves computational and experimental studies to develop methods capable of accurately predicting condensed-state chemical equilibria. Thermodynamic property computation for isolated molecules as well as condensed-state computational model development are thus central to this work. Currently, the specific computational goal is to assemble a single force-field program for calculating thermodynamic properties that combines accuracy and applicability to a wide variety of hydrocarbon and heteroatomic compounds. Specifically, a program is being developed to calculate standard enthalpies of formation and torsional potential energy functions for single carbon-carbon bonds. Recent calculations of torsional energy profiles of various dienes resulted in improvements in calculations of conformer energy differences, barriers to internal rotation, and hindered internal rotational contributions to the thermodynamic functions of the conformers. Experimental work supporting development of this computational model has recently involved calorimetric determination of the standard enthalpy of formation of the Diels-Alder adduct of maleic anhydride/anthracene. Modeling of the condensed phase thus far has involved the study of moderate-size polar molecules such as dimethyl ether. The complications of dealing simultaneously with electrostatic interactions and nonspherical shape have required developing very efficient computational methods. In particular, efficient molecular dynamic packages in the isobaric-isothermal ensemble (N,P,T) are being developed.

Cornell University Ithaca, NY 14853-5201

School of Chemical Engineering

386. *Theory and Simulation of Fluids of Associating Chain Molecules*

Gubbins, K.E. **\$250,000**
Comm. 607-255-4385

This work will develop a new equation of state for chain molecules that takes molecular size into consideration. Computer simulations of hard spheres and hard sphere chains with multiple bonding sites will be used to predict phase equilibria and to test the theory. Quantitative predictions are being made for the phase diagrams of binary and ternary mixtures of industrial interest, with components such as alkanes, alcohols, water, and benzene. Later in the research, the adsorption of associating chain molecules at vapor-liquid, liquid-liquid, and solid-liquid surfaces will be studied. New work on fluids in pores is being initiated. Molecular simulations and theoretical calculations are being made to study the adsorption of methane and other simple fluids in porous carbons and other inorganic materials.

387. *Exact Calculations of Phase and Membrane Equilibria for Complex Fluids by Monte Carlo Simulation*

Panagiotopoulos, A.Z. **\$85,000**
Comm. 607-255-8243

The central theme of this project is the investigation of phase equilibria for complex fluids using a novel methodology, Monte Carlo simulation in the Gibbs ensemble. The methodology enables the direct determination of the properties of any number of coexisting fluid phases from a single computer experiment, and is applicable to multicomponent systems with arbitrary equilibrium constraints. Current work focuses on the determination of equilibria in ionic and polymeric systems. The first exact calculation of the critical point and phase envelope for the restricted primitive model for ionic solutions has recently been obtained. The calculations are being extended to asymmetric electrolytes and mixtures of electrolytes and nonelectrolytes. In the area of polymeric systems, a novel methodology has been developed based on insertion of test segments in a dense polymeric melt, that allows the calculation of chemical potentials (and thus phase behavior) for polymers of arbitrary chain length. The results of the simulations are being compared with theoretical models and phenomenological correlations, in order to determine the range of applicability of existing techniques and provide the data necessary for systematic improvements.

388. *Experimental and Theoretical Studies of Dense Fluid Mixtures*

Zollweg, J.A. **\$85,000**
Comm. 607-255-7101

The primary goals of this research are: (1) to carry out a comprehensive thermophysical property measurement program on a few strategic pure fluids and mixtures and (2) to develop methods for correlating, extrapolating, and predicting dense fluid properties using statistical mechanics and intermolecular potential theory. Measurements of interfacial tension have been initiated on binary mixtures

of krypton with argon, methane, and ethane at temperatures from 125 K to the critical line of the mixture using both differential capillary rise and differential bubble pressure techniques. These measurements will be used to provide a definitive test between two corresponding states principles for correlating interfacial tension data, the "density" and "field" variable versions. Molecular dynamics computer simulations of liquid-vapor interfaces in pure fluids and mixtures are being performed to compare with the experiments. Measurement of sound speed in liquids under pressure continues using the pulse echo overlap technique. Currently sulfur hexafluoride is being studied from its triple point up to supercritical temperatures.

Department of Chemistry

389. Reaction and Diffusion in Turbulent Combustion

Pope, S.B. **\$175,000**
Comm. 607-255-4314 **(19 months)**

The overall objective of the project is to provide a better understanding of the coupled processes of mixing and reaction in turbulent combustion. This is to be achieved through three approaches. First, direct numerical simulations (DNS) are being performed of reaction in isotropic turbulence. The reaction scheme is constructed to be as simple as possible while retaining the essential features of non-premixed combustion chemistry. Second, stochastic Lagrangian models of molecular mixing will be constructed, based on the DNS results. Third, turbulent mixing will be studied in terms of molecular motion. Work to date has been entirely on the DNS approach. The reaction scheme to be used has been developed, and the numerical algorithm has been tested and evaluated for simple cases. Full DNS runs will begin shortly.

University of Delaware Newark, DE 19716

Department of Chemical Engineering

390. The Generalized van der Waals Theory of Pure Fluids and Mixtures

Sandler, S.I. **\$64,000**
Comm. 302-451-2945

A computer simulation of model molecules (on a CRAY supercomputer) and a form of the canonical partition function, developed previously and referred to as the generalized van der Waals partition function, has been successfully used to test the basis of current thermodynamic models, and to develop new ones. This work has provided detailed insight into the molecular basis of thermodynamic modeling and local composition effects. In particular, a better understanding of the temperature and density dependence of various terms in the equation of state has been obtained, and new equations have been developed, such as the simplified perturbed hard chain equation. Local composition models based on computer simulations have been used in the generalized van der Waals partition function to obtain new activity coefficient models and equation of state mixing rules. Work is currently under way extending this research to nonspherical chain molecules, and to mixtures of molecules that differ greatly in size and functionality. Research completed on

the effect of molecular polydispersivity on phase equilibrium has resulted in new, more efficient descriptions of mixtures as varied as petroleum reservoir fluids and polymer solutions used in biological separations. A polymer fractionation phenomenon in this work has been discovered and has been experimentally verified. Work is continuing on the use of *ab initio* molecular orbital calculations to improve group contribution prediction methods.

University of Illinois at Chicago Chicago, IL 60680

Department of Chemical Engineering

391. Evaluation of Mixing Rules for Viscosity and Thermal Conductivity Using Nonequilibrium Molecular Dynamics

Murad, S. **\$68,000**
Comm. 708-996-5593

A method developed previously to study the thermal conductivity of nonspherical fluids (using the method of nonequilibrium molecular dynamics) was used to investigate the contributions to thermal conductivity of internal rotational degrees of freedom. In many engineering correlations these contributions are assumed to be only temperature-dependent, apparently without any theoretical justification. Studies on diatomics have shown clearly that these contributions are indeed density-dependent. The studies are now being extended to more complex molecular structures, such as benzene, to examine this question further. Further studies on thermal conductivity of continuous, semicontinuous, and multicomponent discrete mixtures have been conducted with several distributions such as linear, Gaussian, and Unsymmetric. Results for such systems confirmed the previous preliminary results, that two-component characterizations of such mixtures was satisfactory, and significantly better than one-component characterization.

Johns Hopkins University Baltimore, MD 21218

Department of Chemical Engineering

392. Prediction of Thermodynamic Properties of Coal Derivatives

Donohue, M.D. **\$85,000**
Comm. 301-338-7761

It is difficult to predict the properties of streams found in coal processing operations. There are two primary reasons for this difficulty. The first is that the species encountered in coal processes are quite complex in both their physical structure and in terms of their intermolecular potential functions. In contrast to the species found in petroleum-based processes, a wide variety of compounds are encountered in coal-derived products with more aromatic species and more compounds with functional groups containing oxygen, nitrogen, and sulfur. The second difficulty concerns a lack of knowledge of multicomponent mixtures—especially when the species involved differ significantly. There are few thermodynamic theories (either

equation of state or activity coefficient) that can yield accurate predictions of even binary phase behavior without the use of large binary interaction parameters. In general, there is no reason to believe that these parameters will be valid in ternary and multicomponent mixtures without additional ternary and quaternary parameters. A multifaceted approach to addressing these problems is being taken. A semitheoretical equation of state has been developed which attempts to take into account polarity, hydrogen bonding, and molecular size. This equation of state has been systematically evaluated against experimental data for a wide variety of compounds and mixtures. From the lessons learned concerning the successes and failures of this equation, molecular simulations have been devised to help guide the next generation of theory. Current efforts are concerned with simulations at low densities where, it appears, many properties do not scale linearly with molecular size.

**University of Maryland
College Park, MD 20742**

Institute for Physical Science and Technology

393. Thermophysical Properties of Supercritical Fluids and Fluid Mixtures
Sengers, J.V. **\$90,000**
Comm. 301-405-4805

This research is concerned with thermodynamic and transport properties of fluids and fluid mixtures. By extending the Landau-Ginzburg-Wilson theory of critical phenomena, an equation of state has been constructed that represents the global behavior of thermodynamic properties in the critical region including the crossover to regular behavior far away from the critical point. The theory has been applied to represent the thermodynamic properties of a variety of fluids including carbon dioxide, steam, ethane and most recently R134a, a possible refrigeration fluid. The theory has been extended to binary fluid mixtures and is being applied to mixtures of carbon dioxide and ethane. In addition, by extending the mode-coupling theory of dynamic critical phenomena, a scientific representation of the global behavior of the transport properties of fluids has been obtained. New, accurate thermal-conductivity data obtained in collaboration with scientists at the University of Amsterdam are in agreement with this theory. Measurements of the thermal conductivity of mixtures of carbon dioxide and ethane near the vapor-liquid critical line are in progress.

**University of Massachusetts at
Amherst
Amherst, MA 01003**

Department of Chemical Engineering

394. Theoretical Studies of Solid-Fluid Phase Equilibria
Monson, P.A. **\$109,000**
Comm. 413-545-0661 **(16 months)**

This project is concerned with the theory of solid-fluid phase equilibria, especially for systems with anisotropic

intermolecular forces and for mixtures. The main goal of the work is to develop tractable theories that can be applied to problems such as (1) the prediction of the melting line for anisotropic molecules and development of an understanding of the departures from the principle of corresponding states for solid-fluid equilibria; (2) the prediction variations of solubility of solids in liquids with details of the molecular interactions; and (3) the prediction of solid phase miscibility on the basis of the intermolecular forces. The project has two components. In the first component the cell theory of solids will be extended to the cases of nonspherical molecules and mixtures. This will provide free energy and chemical potentials for the solid phase which can then be combined with results from liquid state theories to determine phase equilibrium. In the second component Monte Carlo computer simulations will be used to determine stable crystal structures, free energies, and chemical potentials for various model systems. The simulation results will provide data for rigorous testing of the theoretical predictions and provide physical insight into the development of approximations.

**National Institute for Petroleum and
Energy Research
Bartlesville, OK 74005**

Department of Fuels Research

395. Thermodynamic Properties by Noncalorimetric Methods
Steele, W.V. **\$185,358**
Comm. 918-337-4210 **(24 months)**

This research complements the experimental programs currently in progress at the National Institute for Petroleum and Energy Research (NIPER) for other divisions of the Department of Energy. Those experimental programs are focused on the calorimetric determination of thermodynamic properties of key polynuclear heteroatom-containing aromatic molecules. This program focuses on the noncalorimetric determination of thermodynamic properties through the extension of existing correlation methodologies and through molecular spectroscopy with statistical mechanics. Important advances made in the program to date include: (1) group-contribution parameters derived for estimation of thermodynamic properties for polycyclic aromatic nitrogen-, oxygen-, and sulfur-containing compounds. Group parameters for nitrogen heterocycles were derived and used to estimate properties for several benzoquinolines not studied calorimetrically. The parameters allow calculation of thermodynamic properties for all pyrrolic and pyridinic polyaromatics. (2) A long pathlength, far-infrared sample cell was operated successfully in the collection of vapor-phase spectra of polycyclic compounds (up to three rings) with low vapor pressure. Previously only one- and two-ring molecules could be studied. (3) A method was developed to predict the vibrational frequencies of two- and three-ring polycyclic molecules to an accuracy sufficient for identification of fundamental vibrations in experimental spectra. (4) A method developed in this project to calculate the kinetic energy expansions as a function of the coordinate for the ring-puckering, ring-twisting (in-phase), and ring-twisting (out-of-phase) modes for molecules containing large amplitude anharmonic vibrations was applied in a study of

9,10-dihydroanthracene. These results were recently verified in the study of the fluorescence and absorption spectra of jet-cooled 9,10-dihydroanthracene. In molecules with large-amplitude anharmonic vibrations, research in this project has shown that the direct summation of calculated energy levels to obtain the partition function for the vibration must be extended to near $10,000\text{ cm}^{-1}$ before the contribution from subsequent levels becomes negligible. (5) Correlation of critical properties for heteroatom-containing polycyclic aromatic compounds was continued. Key to the correlation are new experimental values obtained in complementary projects at NIPER. This is an initial step in the development of a new theoretical vapor-pressure equation applicable between the critical and triple-point pressures.

**National Institute of Standards and
Technology, Boulder
Boulder, CO 80303**

Thermophysics Division

**396. *Integrated Theoretical and Experimental
Study of the Thermophysical Properties of
Fluid Mixtures***

Ely, J.F. **\$281,000**
Comm. 303-497-5467

The major objective of this research is the development of theoretically based predictive models for complex fluid mixtures. The research consists of three main elements: (1) development of predictive procedures for the properties of fluids and fluid mixtures, (2) basic understanding of fluid behavior through advances in theory and computer simulation, and (3) development of theoretically based correlations. The study includes the acquisition and analysis of neutron scattering data which are being used to explore the microstructure of complex fluids. These measurements are being used to support theoretical and modeling efforts. Emphasis is placed on development of predictive models in the form of computer codes which can be readily transported to engineering users and which are easily incorporated into industrial design packages. In the development of predictive procedures, advanced corresponding states theories are being used, including the extended corresponding states concept and field space corresponding states ideas. Computer simulations will be performed for systems in equilibrium and out of equilibrium (e.g., under shear). The computer simulation results are used to test and extend the theoretically based models. Finally, models of near critical transport properties of mixtures are being developed using crossover theory and field space concepts.

**North Carolina State University
Raleigh, NC 27695-7905**

Department of Chemical Engineering

**397. *Theoretical Treatment of the Bulk and
Surface Properties of Fluids Containing
Long, Flexible Molecules***

Hall, C.K. **\$222,167**
Comm. 919-737-3571 **(24 months)**

This research program is designed to enhance understanding of the behavior of fluids and fluid mixtures containing chain-like molecules in bulk and in pores. The first objective of this research is to develop an equation of state which is capable of predicting the experimentally observed thermodynamic properties, including phase equilibria, of fluids and fluid mixtures containing chain-like molecules ranging in length from alkanes to polymers. The approach here will be to extend the Generalized Flory theories to fluids and fluid mixtures containing chain molecules whose segments are subject to both attractions and repulsion and to very long chain systems. The second objective of this research is to provide an understanding, on a molecular level, of the properties of chain fluids in narrow pores. The approach here will be to develop a new method for the computer simulation at constant chemical potential of chain fluids in pores and then to use this technique to predict adsorption isotherms for model chain fluids in pores whose walls interact with the confined species. The theories resulting from this research could eventually serve as the foundation upon which to build correlations of thermophysical properties of petroleum, natural gas, polymer solutions, polymer melts, and polymer blends in bulk, at surfaces, and in pores.

**University of Pennsylvania
Philadelphia, PA 19104-6393**

Department of Chemical Engineering

**398. *Thermodynamics and Transport in Micro-
porous Media***

Glandt, E.D. **\$97,000**
Comm. 215-898-6928

This is a computational project concerned with the structural and topological properties of model porous materials, and with how these determine the transport behavior of a medium and the partitioning of compact and of chain macromolecular solutes into it. Complete sets of geometric, connectedness, and transport information will be generated on low-porosity sintered structures by random-walk, first-passage methods. New acceleration techniques have been developed for the solution of the diffusion equation within random boundaries rather efficiently. Percolation phase diagrams for both the solid and pore phases will be mapped for varying degrees of interpenetrability of the sintered particles constituting the body. The determination of the distribution coefficient for random flight chain molecules in the pore space (including the case of branched polymers) can be computed with analogous methods. The physical adsorption of repeat units of the polymer onto the walls of the solid matrix is also considered.

Princeton University
Princeton, NJ 08544-5263

Department of Chemical Engineering

399. Molecular Interactions in Dilute Supercritical Mixtures: Molecular Dynamics Investigation
Debenedetti, P.G. **\$52,545**
Comm. 609-258-5480

This project will investigate the interactions between solute and solvent molecules, as well as between solute molecules, in dilute supercritical mixtures. Integral equations and molecular dynamics computer simulations are used to understand how differences in size, shape, and interaction energy between the solute and the solvent (molecular asymmetry) influence short-range and long-range behavior in the supercritical region. The overall goal is to develop a fundamental, molecular-based understanding of the behavior of highly asymmetric mixtures in which the solvent is a supercritical fluid. Currently under study is (1) how molecular asymmetry controls the extent to which a mixture can be considered dilute when the solvent is near its critical point and (2) the nature of solute-solute interactions in highly dilute mixtures when the solvent is near its critical point.

Purdue University
West Lafayette, IN 47907

School of Chemical Engineering

400. Gas-Liquid-Liquid Equilibria in Mixtures of Water, Light Gases, and Hydrocarbons
Chao, K.-C. **\$80,000**
Comm. 317-494-4088

The Augmented BACK equation of state that was developed in this project was further simplified to contain only 8 terms and 16 fitting constants for the polar pressure which required 57 terms in a previous version of the equation. This further simplified equation appears to retain the accuracy of vapor pressure and liquid density calculations for polar fluids and the accuracy of fluid phase equilibrium calculations for mixtures of polar fluids. A new method for the simulation of free energy of a liquid has been developed by MC sampling of the Boltzmann factor functional to avoid the generally recognized pitfalls of a direct calculation of this quantity. The new method depends neither on test particle, nor particle insertion (as in the Gibbs ensemble method), making it well suited for polyatomic molecules. It becomes possible to simulate the chemical potential of the atoms of a polyatomic molecule. The statistical mechanics of group contribution can be developed. The simulation of Henry's constant of a light gas dissolved in the liquid of a polyatomic substance is being carried out.

Stanford University
Stanford, CA 94305-5025

Department of Chemical Engineering

401. Fundamental Studies of Fluid Mechanics and Stability in Porous Media
Homsy, G.M. **\$118,375**
Comm. 415-723-2419 **(24 months)**

This research treats problems in flow and transport in porous media of interest in energy recovery processes. A major focus is the study of instabilities that occur during displacements that are driven by differences between the properties of the displaced and displacing fluids. Both experiments and large-scale simulations are carried out in these studies. Either density differences (when coupled with gravity) or viscosity differences may drive such instabilities, and the fluids may be either immiscible or miscible. Current research is focused on the description of miscible fingering in the presence of anisotropic dispersion, such as occurs in porous materials or model Hele-Shaw cells. Results indicate that a new mechanism, associated with the merging or coalescence of fingers, becomes dominant when the anisotropy is large. The ability of two-dimensional simulations to model the averaged macroscopic behavior seen in experiments, which are necessarily three-dimensional in nature, is currently being assessed in two ways. First, two-dimensional predictions are being compared with experimental results. Second, the calculations have been recently extended to three dimensions. These will be the first reliable three-dimensional calculations at high Peclet numbers. The phenomena of tip-splitting and coalescence in three-dimensions will be studied in the near future.

State University of New York at Stony Brook
Stony Brook, NY 11794

Department of Chemistry

402. Thermophysical Properties of Fluids and Fluid Mixtures
Stell, G.R. **\$112,000**
Comm. 516-632-7899

Transport coefficients from the most highly developed version of kinetic theory (KVTIII) have been compared with the coefficients found from computer experiments and simple-fluid experiments over a wide range of temperatures in the dense-fluid regime. The agreement is good; the approach appears to represent the most quantitatively successful analytic "first-principles" approach yet developed. An analysis of the linearized theory, which facilitates comparison with important earlier work by others, has also been made. A detailed study of the viscosity of a polydisperse solute (not necessarily dilute) in a monodisperse solvent has also been conducted. Finally, a mathematically rigorous study of a family of generalized KVTs (that includes KVTIII) has been initiated. With respect to equilibrium results, a general theory of liquids in pores was introduced via an integral-equation approach to the problem. These initial results focused on the hard-sphere-fluid model in hard-walled pores. A closely related

theory of liquid structure in the vicinity of membrane and vesicle surfaces was also developed. An equilibrium theory of molecular association and of the association of weak electrolytes has been developed and applied to the case of diatomics that dissociate into either monatomic atoms or ions, depending upon the details of the model. Extensive numerical results for association constants and related quantities have been obtained.

**University of Virginia
Charlottesville, VA 22903-2442**

Chemical Engineering Department

- 403. Theoretical and Experimental Study of Mixed Solvent Electrolyte Systems**
Cummings, P.T.; O'Connell, J.P. **\$110,000**
Comm. 804-924-6248

The objective of this project is to develop fundamentally based predictive theories for the thermodynamic properties and phase equilibria in mixed solvent and mixed salt electrolyte systems. The emphases in the current year are: molecular simulation of vapor-liquid phase equilibria in alcohol/water, water/salt, and alcohol/water/salt systems; molecular simulation of supercritical aqueous systems; development of statistical mechanical theory of mixed solvent and mixed salt electrolyte solutions; and additional experimental measurements of phase equilibria in mixed solvent electrolyte systems.

**University of Wisconsin at Madison
Madison, WI 53706**

Department of Chemical Engineering

- 404. Interphase Transport and Multistage Separations**
Stewart, W.E. **\$85,000**
Comm. 608-262-0188

This project deals with the mathematical modeling of mass transfer processes, including transport theory, computational methods, and correlations of system performance. Recent developments include an efficient simulation scheme for steady-state sieve tray simulations and a promising set of correlations for the use of this scheme in process predictions. A comprehensive investigation of several enhancements of Newton-like methods has been completed. Work continues on the structure of mass-transport boundary layers in turbulent flows with stationary boundaries.

**Yale University
New Haven, CT 06520**

Department of Mechanical Engineering

- 405. Computational and Experimental Study of Laminar Premixed and Diffusion Flames**
Smooke, M.D.; Long, M.B. **\$123,000**
Comm. 203-432-4344

The objective of this work is to understand the effects of detailed chemistry and mass transport on the structure and extinction of premixed and nonpremixed hydrocarbon flames. The work considers both a computational and an experimental approach. Computationally, the coupled nonlinear elliptic equations are solved for the conservation of mass, momentum, species balance, and energy in two-dimensional axisymmetric geometries with adaptive finite difference methods. The model employs both detailed transport coefficients and finite rate chemistry. The computational work focuses on the effects of boundary conditions, reaction mechanisms, and burner configurations on the structure of methane-air flames. The experimental portion of the work applies nonintrusive spontaneous Raman spectroscopy to image simultaneously the major species in the flame. Laser induced fluorescence is used to measure trace radical species. The research goals include the refining of the experimental techniques and the accuracy with which such measurements are made along with the development of a more fundamental understanding of the important fluid dynamic and chemical interactions that occur in such systems.

**Small Business Innovation
Research**

The following projects were funded during FY 1991 by the Small Business Innovation Research (SBIR) Program Office in response to a topic submitted by the Division of Chemical Sciences to the annual SBIR Solicitation.

The Phase I projects are funded for 6½ months and are designed to evaluate the merits and feasibility of the ideas proposed. Proposals are considered as a result of a solicitation and awards are made after competitive evaluation. New Phase I grant information arrived too late for inclusion in this section of the summary book. A list of them appears in the back of the book.

The Phase II projects are funded for two years and constitute the principal research and development effort aimed at proving the feasibility of the concept or carrying the process or product to the point where it can be commercialized. They are continuations of Phase I projects. Again, awards are made on the basis of competitive evaluation.

Chromex, Inc.
Albuquerque, NM 87107

406. The Development of a Multiple-Input Spectrometer for Process Monitoring Applications

Gobeli, G.W. **\$499,000**
Comm. 505-344-6270

Recent years have seen significant advances in light detection technology and computer processing power. There are two-dimensional array detectors (e.g., CCD arrays) that are entirely capable of performing as scientific detectors. Modern small computers are capable of handling the vast quantities of data produced almost instantaneously by these detectors. The missing building block in the development of a spectrometer that can take advantage of these developments is an optical system capable of two-dimensional imaging. A proprietary method of producing high quality aspheric optics will be used to produce a high resolution stigmatic flat-focal-field spectrograph that, when coupled with array detection, can be the basis for a multiple fiber-optic input spectrophotometer. The resulting multiple spectrochemical measurements can be used to simultaneously determine target analyte concentrations at several locations. Such an application might be combustion diagnostics where numerous locations within a combustion chamber could be simultaneously monitored or a plasma reactor where spectral analysis could be made simultaneously at a number of discrete spatial locations within the reactor.

Membrane Technology & Research, Inc.
Menlo Park, CA 94025

407. Ultrathin Metal Membranes

Athayde, A.L. **\$500,000**
Comm. 415-328-2228 **(24 months)**

The Phase I program demonstrated the feasibility of preparing ultrathin composite metal membranes with

high selectivity and high hydrogen flux. The membranes consist of a permselective palladium/silver layer on a microporous polymer support layer, overcoated with a polymer sealing layer. The Phase II program will bring ultrathin composite metal membranes to the point of readiness for pilot-scale testing. With palladium/silver membranes as the model system techniques for membrane preparation will be refined with the goal of a continuous production process for rolls of membrane materials. Membranes will be evaluated for selectivity and flux in a bench-scale test unit, using typical industrial gas mixtures. The problems of membrane poisoning will be investigated. Based on these results, a pilot scale membrane gas separation system will be designed.

Southwest Sciences, Inc.
Santa Fe, NM 87501

408. A Novel Mass Spectrometer for Combustion Studies

Bomse, D.S. **\$499,871**
Comm. 505-984-1322 **(24 months)**

This project uses a novel scheme, ionization energy modulation, to increase the amount of chemical information obtained from mass spectroscopy and uses the added information to support automated computerized deconvolution of the mass spectra of combustion mixtures. The Phase I research successfully demonstrated the ability of the method to enhance the information content obtainable from the mass spectra. In particular, it clearly distinguished among different species at the same parent ion mass, and could separate isomeric forms of the same compound. In Phase II, a prototype mass spectrometer using ionization energy modulation will be constructed and tested by quantifying the components in complex combustion mixtures above methane/oxygen and butane/oxygen flames.

ADDENDUM

Information on the following grants was received too late for their inclusion in the body of this book.

Chemical Physics

Cornell University
Ithaca, NY 14853

Department of Chemistry

409. *Photochemical Dynamics of Surface Oriented Molecules*
Ho, W. \$185,000
Comm. 607-255-3555

Utah, University of
Salt Lake City, UT 84112

Department of Chemistry

410. *Thermochemistry of Transition Metal Clusters*
Armentrout, P. B. \$125,000
Comm. 801-581-6681

Atomic Physics

Auburn University
Auburn, AL 36849

Department of Physics

411. *Electron Collisions with Positive Ions*
Henry, R. J. W. \$62,000

Kansas, University of
Lawrence, KS 66045

Department of Chemistry

412. *Atomic Physics in Strong Fields*
Chu, S.-I. \$70,000
Comm. 913-864-4094

SBIR PHASE I

Atlantic Applied Research Corporation
Burlington, MA 01803

413. *Enhancement of Membrane Filter Performance by Vibration*
Africk, S. A. \$49,995
Comm. 617-273-2400 (6.5 months)

Bend Research, Inc.
Bend, OR 97701-8599

414. *High Permeability Polymers for Use in Making High-Performance Membranes for Gas and Vapor Separations*
Friesen, D. T. \$50,000
Comm. 503-382-4100 (6.5 months)

CeraMem Corporation
Waltham, MA 02154

415. *Chemically Durable Silica-Zirconia Nanofiltration Membranes*
Goldsmith, R. L. \$50,000
Comm. 617-899-0467 (6.5 months)

**EIC Laboratories
Norwood, MA 02062**

**416. Universal Chemical Vapor Sensors with
Combined Mass and Spectroscopic
Selectivity**

Carrabba, M. M. **\$50,000**
Comm. 617-769-9450 **(6.5 months)**

**Eltron Research, Inc.
Aurora, IL 60504**

**417. Distributed Fiber Optic Sensor for
Reversible Detection of Atmospheric CO₂**

Cook, R. L. **\$49,995**
Comm. 708-898-1583 **(6.5 months)**

**Materials and Electrochemical
Research (MER) Corporation
Tucson, AZ 85706**

**418. Novel C₆₀ Electrodes for Advanced
Electrochemical Sensors**

Loutfy, R. O. **\$50,000**
Comm. 602-574-1980 **(6.5 months)**

**Membrane Technology and Research,
Inc.
Menlo Park, CA 94025**

419. Ultrathin Composite Membranes

Athayde, A. **\$50,000**
Comm. 415-328-2228 **(6.5 months)**

**Moltech Corporation
Stony Brook, NY 11793-3400**

**420. Advanced Biosensors for Analytical
Chemical Measurements**

Hale, P. D. **\$49,874**
Comm. 516-632-7565 **(6.5 months)**

**Southwest Sciences, Inc.
Santa Fe, NM 87501**

**421. Measurement of Combustion Radicals
Using Visible/Near-Infrared Diode Lasers**

Silver, J. A. **\$50,000**
Comm. 505-984-1322 **(6.5 months)**

SPECIAL FACILITIES

The special facilities described on the following pages are supported wholly or partly by the Division of Chemical Sciences. They represent an assembly of unique and/or expensive equipment which would be costly to develop elsewhere. They represent research resources for the general scientific community, and qualified scientists from laboratories outside the host laboratory are encouraged to make use of them. However, any activity that can be carried out through commercially available laboratories is not appropriate for these DOE-supported facilities.

The process by which an off-site scientist can use a facility is discussed in each facility summary. For the National Synchrotron Light Source, the Stanford Synchrotron Radiation Laboratory, and the Combustion Research Facility, see the section "User Mode." For the remaining facilities, see "Collaborative Use," which is a process based on the

need for collaboration by the off-site scientist with one or more in-house staff members.

Each of the facility summaries also gives the names of individuals to contact for further information, a general description of the facility, and a list of technical data on the primary available instrumentation.

The Office of Basic Energy Sciences also supports other facilities not summarized here. Information concerning these can be obtained by contacting Dr. Iran Thomas, Director of Materials Sciences, ER-13, U.S. Department of Energy, Washington, DC 20585.

Budgets for the operation of those facilities specifically funded as Chemical Sciences Facilities (KC-03-01-04) are given below.

Location	Facility	Operating Funds
Brookhaven National Laboratory	National Synchrotron Light Source	\$ 7,000,000
Oak Ridge National Laboratory	High Flux Isotope Reactor	30,390,000
	Radiochemical Engineering Development Center	7,610,000
Sandia National Laboratories, Livermore	Combustion Research Facility	4,300,000
Stanford University	Stanford Synchrotron Radiation Laboratory	11,000,000

4.5-MV DYNAMITRON ACCELERATOR (KC-03-01-03)

Physics Division
Argonne National Laboratory
Argonne, IL 60439

The Argonne Physics Division operates a high-current 4.5-MV Dynamitron accelerator which delivers magnetically analyzed beams of most atomic ions and many molecular ions. Among the unique facilities associated with the Dynamitron are (1) a beam line capable of providing "supercollimated" ion beams that permit angular measurements to accuracies of 0.1 mrad, (2) a beam-foil measurement system capable of measuring lifetimes to a few tenths of a nanosecond, (3) a 28-inch-diameter general-purpose scattering chamber, (4) a laser-ion beam system where an argon pumped dye laser beam is coaxial with the ion beam, (5) a variety of electrostatic and magnetic electron spectrometers, (6) large-area multiwire proportional counters capable of detecting up to eight particles simultaneously with submillimeter position and subnanosecond time resolution, and (7) a postacceleration chopper system giving beam pulses with widths that can be varied from 1 ns to several ms at repetition rates variable up to 8 MHz. A VAX 11/750 computer system with direct links to Argonne's central computing facility is used for on-line data acquisition, analysis, and the control of experiments.

COLLABORATIVE USE

Visiting scientists use the accelerator either in collaboration with Argonne investigators or as independent groups.

PERSON TO CONTACT FOR INFORMATION

E. P. Kanter Phone: Comm. (708) 972-4050
Physics Division or FTS 972-4050
Argonne National
Laboratory
9700 South Cass Avenue
Argonne, IL 60439

TECHNICAL DATA

Range of terminal voltages attainable	0.3 to 4.8 MV
Range of ion beam currents attainable	10 aA to 500 μ A
Monatomic singly charged ion beams available	Most elements
Monatomic multiply charged ion beams available	Rare gases, transition metals
Typical molecular-ion beams available	H_2^+ , H_3^+ , HeH^+ , CH_n^+ , $C_2H_n^+$, $C_3H_n^+$ ($n = 0 - 5$), CO^+ , O_2^+ , etc.
Pulse mode (postchopper)	
Pulse width	1 ns to 10 ms
Repetition rate	0 MHz to 8 MHz

PREMIUM COAL SAMPLE PROGRAM (KC-03-02-01)

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

The purpose of the Premium Coal Sample Program is to provide the coal science research community with long-term supplies of a small number of premium coal samples that can be used as standards

for comparison. The premium coal samples produced from each coal and distributed through this program are as chemically and physically identical as possible, have well-characterized chemical and

physical properties, and are stable over long periods of time. Coals were mined, transported, processed into the desired particle and sample sizes, and packaged in environments as free of oxygen as possible while maintaining the natural moisture content in order to ensure that the coals will be in as pristine and stable a condition as possible.

AVAILABILITY

The first samples became available in mid-1985, and the set of eight samples was completed in early 1987. These samples are available to research personnel at a nominal replacement cost. A very limited quantity of lump coal, stored under similar inert conditions, is available on special request for special physical property measurements. Distribution of these samples is guided by policies

established with the help of a users advisory committee. The processing facility may be available for occasional processing of special samples. More than 520 shipments totaling over 14,000 ampoules have been made. A Users Handbook is updated annually and available from the Manager.

PERSON TO CONTACT FOR INFORMATION

Dr. Karl S. Vorres	Phone: Comm. (708) 972-7374
Chemistry Division,	or FTS 972-7374
Bldg. 211	FAX (708) 972-4470
Argonne National	
Laboratory	
9700 South Cass	
Avenue	Telex: TWX 910-258-3285
Argonne, IL 60439	USDOE-CH ARGN

PULSE RADIOLYSIS FACILITY (KC-03-01-01)

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

The Argonne linear electron accelerator was designed for chemical research. The moderate energy of the electron accelerator (maximum energies of 21 MeV transient mode, 14 MeV steady state) allows the use of the electron beam for the generation of transient species without nuclear activation. The pulse width can be varied from 25 ps to 10 μ s. In addition, a 5-ps pulse with the same peak current as the 25-ps pulse has been developed. In liquids, transient concentrations up to 20 μ M can be generated with the 25-ps pulse, and concentrations in excess of 10 mM can be generated with the longest pulse. Instrumentation for measurement of chemical processes allows kinetic spectrophotometric absorption and emission and fast conductivity measurements. A 2-ps streak camera with custom software is available for fast emission measurements. Simultaneous multiwavelength kinetic spectrophotometric measurements are possible, and very high time resolution measurements that use the short pulse capability of the LINAC can also be made, both in absorption and emission. All data acquisition equipment is computer interfaced to

provide accurate data reduction. Sample preparation and handling facilities are available for solid, liquid, and gaseous samples.

COLLABORATIVE USE

Collaborative experiments can be arranged with appropriate staff scientists.

PERSON TO CONTACT FOR INFORMATION

Charles D. Jonah	Phone: Comm. (708) 972-3471
Chemistry Division	or FTS 972-3471
Argonne National	or FAX (708) 972-4993
Laboratory	
9700 South Cass Avenue	
Argonne, IL 60439	

TECHNICAL DATA

Energy		Current/pulse	
Transient mode	21 MeV	Transient mode	20 A peak
Steady-state mode	14 MeV	Steady-state mode	1.5 A peak
Average current	200 μ A (maximum)	Picosecond pulse	25 nC (charge per pulse)
Pulse repetition rate	Single pulse to 800 pps (800 pps not possible for all pulses)	Picosecond (5 ps)	6 nC
		Pulse width	5 ps
			25 ps
			4 to 100 ns
			15 to 10 μ s steady state mode

NATIONAL SYNCHROTRON LIGHT SOURCE (KC-03-01-04)

Brookhaven National Laboratory
Upton, NY 11973

The National Synchrotron Light Source (NSLS) is the nation's largest facility dedicated to the production of synchrotron radiation. The facility has two electron storage rings: a vacuum ultraviolet (VUV) ring, which operates at an electron energy of 750 MeV designed for optimum radiation at energies between 10 eV and 1 keV, and an X-ray ring, which operates at 2.5 GeV to optimize radiation between 1 keV and 20 keV. The X-ray ring accommodates 30 experimental ports and the VUV ring accommodates 17. Each of these ports is split into two to four beam lines. By the end of 1991, the Light Source will have 85 operational experimental beam lines. Of these 10 lines are dedicated to beam diagnostics and R&D.

From their conception, the designs of the storage rings included long, field free straight sections for special radiation sources (wigglers and undulators). The two straight sections on the VUV ring and the five available on the X-ray ring now have a variety of wigglers and undulators providing radiation that is anywhere from one to several orders of magnitude brighter than the comparable bending magnets. These devices are the sources for a wide variety of experiments in the biological, chemical, and materials sciences.

Photons, as a probe, provide information about the electronic and atomic structures of interest to the chemical, biological, and materials sciences. The techniques fall broadly into two areas: spectroscopy and scattering. At the NSLS, they are applied to forefront research: imaging in both real space (e.g., X-ray microscopy, tomography, angiography)

and reciprocal space (e.g., protein crystallography, X-ray topography), surface science (e.g., photoemission surface diffraction, infrared spectroscopy), and recently magnetism (e.g., magnetic X-ray scattering, spin polarized photoemission). These are but a few of the exciting research opportunities at the NSLS. By January 31, 1991, 2250 scientists from 292 universities, laboratories, corporations, and foreign institutions were using the research tools available at the NSLS. This is an increase of 900 Users and 78 institutions over January 1990.

Proprietary research can be performed at the NSLS. The DOE has granted the NSLS a Class Waiver under whose terms the Proprietary User is obligated to pay the full cost recovery rate for NSLS usage. In return, the user has the option to take title to any inventions made during the proprietary research program and to treat as proprietary all technical data generated during the proprietary research program. In FY 1990, the total number of corporations participating in proprietary research at the Light Source was ten.

USER MODES

The policy for experimental utilization of the NSLS is designed to enable the scientific community to cooperate in establishment of comprehensive long-range experimental programs. Beam lines are either constructed by Participating Research Teams (PRTs), Insertion Device Teams (IDTs), or by Brookhaven staff members. The institutional representation on the PRTs and IDTs totals 75. Each PRT and IDT is entitled to up to 75% of their beam line's operational time for a three-year term. The

remaining beam time is made available to scientists categorized as "General Users."

General Users are scientists interested in using existing NSLS facilities for experimental programs. The NSLS runs three scheduling cycles per year. Access to the facility is through a proposal system. Proposals are reviewed by NSLS staff for technical feasibility, safety, and personnel resources and checked by the cognizant beam line personnel for conformance to the beam line's capabilities. General User proposals are subject to review by a Proposal Study Panel. All beam line/time allocations are assigned by the NSLS General User Oversight Committee. Liaison and utilization support is provided to the General User by the cognizant beam line personnel. One thousand seven hundred and thirty-three days of beam time were allocated to General Users during FY 1990.

A program is available to support faculty/student research groups performing experiments at the NSLS. The program is designed to encourage new users to the facility and defray expenses incurred

during exploratory visits to BNL and while conducting initial experiments at the Light Source. It is aimed at university users having only limited grant support for their research. Eighty-six faculty/student research teams representing 37 universities participated in this program in FY 1990. During this period, 12 universities were added to the list of over 100 institutions who have participated in this program since 1984.

PERSON TO CONTACT FOR INFORMATION

Susan White-DePace NSLS, Bldg. 725D	Phone: Comm. (516) 282-7114 or FTS 666-7114
Brookhaven National Laboratory Upton, NY 11973	E-mail: swd@bnl.bitnet swd@bnl.gov bnl::swd

TECHNICAL DATA

Facilities	Key features	Operating characteristics
VUV electron storage ring	High brightness; continuous wavelength range ($\lambda_c = 25 \text{ \AA}$); 17 ports	0.75-GeV electron energy
X-ray electron storage ring	High brightness; continuous wavelength range ($\lambda_c = 2.5 \text{ \AA}$); 30 beam ports	2.5-GeV electron energy
Research area	Wavelength range, \AA	Number of instruments
Circular dichroism	1400 to 6000	1
Energy dispersive diffraction	0.1 to 2.5	3
EXAFS, NEXAFS, SEXAFS	0.1 to 250	24
Gas phase spectroscopy/ atomic physics	0.6 to 14.6	3
Infrared spectroscopy	2.5×10^4 to 1.2×10^8	2
Lithography/microscopy/ tomography	0.6 to 15	6
Medical research	0.37	1
Nuclear physics	2.5×10^{-6} to 2.5×10^{-4}	1
Photoionization	0.6 to 12000	5
Radiometry	-	1
Reflectometry	20 to 55	1

TECHNICAL DATA (Continued)

Research area	Wavelength range, Å	Number of instruments
Research & development/ diagnostics	White beam	11
Time resolved fluorescence	1000 to 12000	2
Topography	0.1 to 3	3
Transverse optical klystron	12.5 to 1250	1
VUV & X-ray photoemission spectroscopy	0.3 to 1280	27
X-ray crystallography	0.3 to 6.2	9
X-ray fluorescence	12.4 to 620	1
X-ray scattering/ diffraction	0.1 to 15.5	26

JAMES R. MACDONALD LABORATORY (KC-03-01-03)

Department of Physics
Kansas State University
Manhattan, KS 66506

The laboratory operates a 7-MV tandem accelerator, a 9-MV superconducting linear accelerator (LINAC) and a cryogenic electron beam ion source (CRYEBIS) for the study of ion-atom collisions with highly charged ions. The tandem can operate as a stand-alone accelerator with six dedicated beam lines. The LINAC is operated as a booster accelerator to the tandem. The tandem-LINAC combination has four beam lines available. The CRYEBIS is a stand-alone facility for studying collisions with bare ions at low velocity. The laboratory has a variety of experimental apparatus for atomic physics research. These include recoil ion sources, Auger electron spectrometers, x-ray spectrometers, and a 45-inch-diameter scattering chamber. The laboratory is available to users who require the unique facilities of the laboratory for atomic collision experiments.

COLLABORATIVE USE

Users are encouraged to seek a collaborator on the staff or they may submit a brief proposal to the Laboratory Director.

PERSON TO CONTACT FOR INFORMATION

Patrick Richard, Phone: (913) 532-6783
Director
James R. Macdonald Laboratory
Department of Physics
Kansas State University
Manhattan, KS 66506

TECHNICAL DATA

EN Tandem

Beams	Most elements
Terminal voltages	0.3 to 7 MV
Output currents	Up to 10 μ A, depending on the ion species and the charge state
Repetition rate	DC or 3-ns pulses at rates up to 4 MHz, or 12 MHz operation
Magnet limitations	ME/q ² \leq 150

LINAC Booster

Acceleration field	9 MV
Resonators	Split-ring, super-conducting Nb, operated at 97 MHz
Beam repetition rate	12 MHz with 75% of beam bunched
Mass limitation	$M < 100\mu$ due to injection energy

CRYEBIS

Beams	Bare ions of C, N, O, F, Ne, and Ar
Beam energy	A few to 200 keV/q
Output currents	10^5 to 10^8 part/s

PULSE RADIOLYSIS FACILITY (KC-03-01-01)

Notre Dame Radiation Laboratory
University of Notre Dame
Notre Dame, IN 46556

The Notre Dame pulse radiolysis facility is based on a 5-ns electron pulse from an 8-MeV linear accelerator. It is fully instrumented for computerized acquisition of optical and conductivity information on radiation chemical intermediates having lifetimes of 10 ns and longer. An excimer laser/dye laser combination is available for use at the pulse radiolysis facility for double-pulse experiments involving photolysis of radiolytic transients. Energies of ~400 mJ at 308 nm and ~50 mJ at various near-UV and visible wavelengths are available. Detectors having response times of ~2 ns are available. For typical optical absorption studies, where one produces $10^{-5}M$ of intermediates, spectral and kinetic information can be obtained on species having extinction coefficients in excess of $100 M^{-1} cm^{-1}$. Conductometric methods in aqueous solution cover the pH range of 3 to 11. Data are recorded digitally and stored in magnetically readable form for rapid off-line examination of spectral and kinetic details.

COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists or by a proposal to the laboratory director.

PERSON TO CONTACT FOR INFORMATION

J. Bentley, Assistant Director	Phone: Comm. (219) 239-6117
Notre Dame Radiation Laboratory Notre Dame, IN 46556	

TECHNICAL DATA

Electron source	8-MeV linear accelerator
Operating mode	Single pulse, with signal averaging
Data collection	MicroVAX II
Pulse width	5, 10, 20, 50 ns
Time resolution (RC)	2 ns
Pulse current	Up to 1 A
Repetition frequency	$0.2 s^{-1}$
Optical absorption measurements	
Spectral region	210 to 750 nm
Sensitivity	± 0.00002 absorbance
Conductivity	
pH range	3 to 11
Sensitivity	± 5 mhos/cm

EN-TANDEM (KC-03-01-03)

Physics Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

The EN-Tandem is operated primarily as an atomic physics facility. The highest terminal voltage is 6.5 MV. A wide variety of ion species is available. Two 90° magnets with a stripper (gas or foil) between them follow the accelerator so that a range of charge states is available for any ion at a given energy. Available facilities include (1) an ~14-meter flight tube with the capability of doing very small angle scattering and detecting individual charge states; (2) high-resolution Auger-electron spectrometer; (3) an Elbeck magnetic spectrograph with position sensitive detectors; (4) Si(Li) detectors and a curved crystal spectrometer; (5) data acquisition and analysis is performed using a CAMAC-based VAX-11/750 computer system.

COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists or by a research proposal to the EN-Tandem manager.

PERSON TO CONTACT FOR INFORMATION

P. F. Dittner Phone: Comm. (615) 574-4789
Bldg. 5500 or FTS 624-4789
Oak Ridge National
Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6377

TECHNICAL DATA

Beams	Most elements
Terminal voltages	0.3 to 6.5 MV
Source beam currents	Several hundred nA to several μ A
Output currents	Up to 2 μ A, depending on the ion species and charge state
Repetition rate	DC only
Magnet limitations	ME/q ² \leq 80

HIGH FLUX ISOTOPE REACTOR (KC-03-01-04)

Research Reactors Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

The prime purpose of the High Flux Isotope Reactor (HFIR) is to make research quantities of transuranium isotopes. Californium-252 is also produced as a by-product but is made available for the fabrication of neutron sources. These materials are produced in the flux trap in the center of the HFIR fuel element where a thermal-neutron flux of 3×10^{15} neutrons/(cm² · sec) is available to irradiate the curium target material. The HFIR is a beryllium-reflected light-water-cooled and -moderated, flux-

trap reactor with a design power level of 85 MW. It burns 93% enriched ²³⁵U fuel in aluminum-clad plates. Additional irradiation facilities are provided in the beryllium reflector around the fuel element to increase the production rate of the heavy isotopes.

The HFIR also has, as a secondary purpose, the performance of diverse irradiations, tests, and experiments which benefit from the exceptionally

high neutron flux available. In the fuel element flux trap, a hydraulic-rabbit tube provides access to the maximum thermal-neutron flux in the reactor for short-term irradiations, and other positions are ideal for fast-neutron irradiation-damage studies. The beryllium reflector contains numerous experiment facilities with thermal-neutron fluxes up to 1×10^{15} neutrons ($\text{cm}^2 \cdot \text{sec}$). These facilities can accommodate static experimental capsules, complex fuel-testing engineering loops, and special experimental isotope irradiations, the targets for which are prepared by the Oak Ridge National Laboratory or other qualified users. Four beam tubes are used for neutron-diffraction experiments, and a small-angle neutron scattering facility sponsored by the National Science Foundation is available for use by

researchers from universities, industry, and other national laboratories. Management of this facility has been transferred to the Assistant Secretary for Nuclear Energy. The funding remains in the Office of Energy Research.

PERSON TO CONTACT FOR INFORMATION

B. L. Corbett Phone: Comm. (615) 574-7001
Research Reactors or FTS 624-7001
Division
Oak Ridge National
Laboratory
P.O. Box 2008
Oak Ridge, TN 37831

RADIOCHEMICAL ENGINEERING DEVELOPMENT CENTER (KC-03-01-04)

Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

The objective of this program is to supply transplutonium elements for use in research. This involves operation of the Radiochemical Engineering Development Center (REDC), which is the distribution center for the DOE heavy-element research program. Target rods are fabricated at REDC, irradiated in the High Flux Isotope Reactor (HFIR), and processed at REDC for separation, recovery, and purification of the heavy actinides up through ^{257}Fm . Since their construction in the mid-1960s, REDC and HFIR have provided the western world's supply of elements beyond curium (atomic number 96), either directly or by furnishing starting materials for further nuclear-synthesis reactions. The transuranium element isotopes produced in the REDC are used nationally and internationally to study the basic physics and

chemistry of the transuranium elements. They are also being used in research and development programs relating to environmental effects, biological effects, and waste isolation. Management of this facility has been transferred to the Assistant Secretary for Nuclear Energy. The funding remains in the Office of Energy Research.

PERSON TO CONTACT FOR INFORMATION

L. J. King Phone: Comm. (615) 574-7071
Chemical Technology or FTS 624-7071
Division
Oak Ridge National
Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6384

COMBUSTION RESEARCH FACILITY (KC-03-01-04)

Sandia National Laboratories, Livermore
Livermore, CA 94551-0969

Current activities at the Combustion Research Facility (CRF) supported by the Division of Chemical Sciences emphasize the development and the applications of new diagnostic techniques to the study of basic flame processes, research in fundamental chemistry in combustion, as well as analytical studies of reacting turbulent flows. (These programs are individually described elsewhere in this publication.) The active program of visitors to the facility, including senior researchers, graduate students, and postdoctoral researchers supported through the Chemical Sciences Division, is described below.

Facility support, through the Chemical Sciences Division, includes operation and continued development of the CRF central lasers. Several are available. The tunable dye laser (Diana) is used by Sandia staff and visiting scientists for single-shot temperature, density, and species concentration measurements, and for two- and three-dimensional imaging of turbulent flames. A multipurpose laser system (Sirius) consists of a frequency-doubled Nd:YAG laser and a pulse-amplified ring dye laser. When the Nd:YAG laser is operated in single-axial mode in combination with the ring dye laser, the spectral resolution for CARS and other nonlinear spectroscopy experiments (performed in any of the CRF laboratories via the beam distribution system) is as small as a few thousandths of a wave number. Sirius is used also for CARS measurements in flames with large luminous backgrounds (e.g., heavily sooting flames or flames laden with coal particles). A third central laser (Dyeblander) consists of a frequency-doubled Nd:YAG laser and is used routinely to pump dye lasers in user laboratories throughout the CRF.

In addition, DOE/Conservation sponsors programs at the CRF in combustion technologies and materials processing by design, DOE/Fossil supports programs in coal combustion and related diagnostics development, DOE/BES Engineering Science supports advanced analysis of turbulent flows, DOE/ER Applied Mathematical Sciences supports nonlinear analysis of combustion systems,

and DOE/BES Materials Sciences supports programs in combustion-related materials research.

Complete facilities for resident and visiting researchers are available: offices for 60 staff, a meeting room accommodating 250 people, a laboratory building housing 18 independent experiments, special facility laser systems, dedicated VAX computers, a network of computer workstations, and access to Cray computers.

In specific instances, proprietary research can be carried out at the CRF. For this type of work, the DOE will be reimbursed on a full cost recovery basis for the use of all CRF resources. Details of a DOE Class Waiver for patent rights are available.

USER MODE

Qualified scientists are encouraged to take advantage of the specialized resources available at the CRF. Prospective participants should submit a brief proposal to the laboratory director. Criteria for selection include technical merit, the extent to which CRF facilities are used, overlap with DOE program objectives, and the availability of specific equipment.

In general, the CRF will host visiting scientists to use the special-purpose lasers, work with resident staff, make use of computers and codes, and set up experiments. Visitors pay for their own salary, travel, housing, meals, and other local expenses. Facility lasers, apparatus, technicians, instrumentation, computers, and support-group services are provided without charge for research that is not proprietary. Research results from nonproprietary projects are expected to be published and disseminated.

For scientists with active government contracts, support for CRF research often can be arranged on an informal basis with the contract manager. There are opportunities for faculty, postdoctoral scientists, and graduate students to obtain Sandia support for combustion-related research at CRF.

PERSON TO CONTACT FOR INFORMATION

Peter L. Mattern, Phone: Comm. (415) 294-2520
Director or FTS 234-2520
Combustion and Applied Research
Sandia National Laboratories
Livermore, CA 94551-0969

or

J. Stephen Binkley, Phone: Comm.
Manager (415) 294-2174
Combustion Sciences or FTS 234-2174
Department
Sandia National Laboratories
Livermore, CA 94551-0969

Low-pressure flames 10 torr to 1 atm
Mass spectrometer sampling probe
LIF detection of radicals

Atmospheric flames Diffusion and premixed flames

Vertical turbulent diffusion flame Open-circuit, induced-draft wind tunnel with co-flowing axisymmetric fuel jet: 30- by 180-cm viewing section to 6000 scfm flow

Combustion bomb Simulated constant-volume engine combustion

Internal combustion research devices Highly repeatable environment for homogeneous charge, diesel combustion, and pulse combustion studies

Experimental diagnostics research facilities Laser fluorescence laboratory

Turbulent flame structure laboratory Rayleigh, Mie, and Raman 2-D imaging

TECHNICAL DATA

Equipment

Key features

Flashlamp-pumped, tunable dye laser Long pulse, high energy, high average power:
2- μ s pulse length
5 J/pulse, 5 Hz
Tunable 440 to 620 nm
0.3-nm bandwidth

Multipurpose pulsed laser system High peak power, high resolution doubled YAG and tunable dye lasers:
Single mode capability
10 to 500 mJ/pulse
10 to 20 ns/pulse

STANFORD SYNCHROTRON RADIATION LABORATORY (KC-03-01-04)

Stanford Synchrotron Radiation Laboratory
Bin 69, P.O. Box 4349
Stanford, CA 94309-0210

SSRL is a national facility for the utilization of synchrotron radiation in materials sciences, chemistry, biology, physics, medical science, and other disciplines. In addition to scientific research utilizing synchrotron radiation, the laboratory program includes the development of advanced sources of synchrotron radiation (e.g., insertion devices for the enhancement of synchrotron radiation, new ring designs) and the development of state-of-the-art instrumentation for the utilization of synchrotron radiation. The radiation comes from both the 3.5 GeV storage ring, SPEAR, and the 15 GeV storage ring, PEP. SPEAR is dedicated to the production of synchrotron radiation. Operation on PEP is parasitic with the high energy physics program. Presently SSRL has 23 experimental stations on 9 beam lines covering the spectrum from 5 to 45,000 eV. Two additional undulator beam lines on PEP provide the world's most brilliant photon beam at X-ray wavelengths. Specialized facilities for protein crystallography and lithography are available.

Specific research performed at SSRL is extremely varied and includes, in the vacuum ultraviolet area: ionization properties of small molecules, structural and electronic properties of microstructures, properties of ultra-thin layers and small clusters, kinetic process in laser materials, lithography and microscopy, and static properties and dynamic processes of chemisorbed gases.

Research in the chemical and biological sciences includes: the structure and function of homogeneous and heterogeneous catalysts, the structure of metal, metal oxide and semiconductor surfaces and their interactions with small molecules, chemical reactivities in the gas phase, the structure of general chemical compounds through EXAFS, multiple wavelength imaging, protein structures and

functions, dynamics and fluctuations in biological systems, the nature of membrane structure and membrane protein interactions, the structure and function of metal site in metalloproteins and metalloenzymes, and medical angiography.

X-ray physics and materials sciences are represented by: structure of amorphous materials, coordination of impurities and alloying species, structures of and phase transitions in surfaces and thin surface layers, kinetics of structural changes in materials, phase transitions at high pressure, structure of crystalline materials, electronic structure of materials through edge absorption studies, fundamental X-ray scattering and absorption physics, and atomic physics.

USER MODE

SSRL is currently used by approximately 650 scientists from 130 institutions in 32 states and 10 foreign countries. Access to the facility is through a refereed proposal system. Proposals are due September 1 and March 1 each year. The booklet "User Guide" available from SSRL contains information pertinent to proposal submittal. To date, 2136 proposals for research have been received. Demand for experimental time is approximately twice that which can be accommodated.

PERSON TO CONTACT FOR INFORMATION

Katherine Cantwell Phone: Comm. (415) 926-3191
Manager, User or FTS 462-3191
Research
Administration
SSRL
Bin 69, P.O. Box 4349
Stanford, CA 94309-0210

CHARACTERISTICS OF SSRL EXPERIMENTAL STATIONS*

	Horizontal angular acceptance, Mrad	Mirror cutoff, keV	Monochromator	Energy range, eV	Resolution $\Delta E/E$	Approximate spot size, hgt \times width, mm	Dedicated instrumentation
Insertion Devices Stations							
Wiggler Lines-X-ray							
End stations							
4-2 (8 pole)							
Focused	4.6	10.2	Double crystal	2,800 to 10,200	$\sim 5 \times 10^{-4}$	2.0 \times 6.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 \times 20.0	
6-2 (54 pole)							
Focused	2.3	22	Double crystal	2,800 to 21,000	$\sim 5 \times 10^{-4}$	2.0 \times 6.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 \times 20.0	
7-2 (8 pole)							
Focused	4.6	10.2	Double crystal	2,800 to 10,200	$\sim 5 \times 10^{-4}$	2.0 \times 6.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 \times 20.0	Six-circle diffractometer
10-2 (31 pole)							
Focused	2.3	22	Double crystal	2,800 to 21,000	$\sim 5 \times 10^{-4}$	2.0 \times 6.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 \times 20.0	
Side stations							
4-1	1.0		Double crystal	2,800 to 45,000	$\sim 5 \times 10^{-4}$	2.0 \times 20.0	
4-3							
Focused	1.0		Double crystal	2,800 to 45,000	$\sim 5 \times 10^{-4}$.5 \times 20	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 \times 20.0	Two-circle diffractometer vertically focusing mirror
7-1	1.0		Curved crystal	6,000 to 13,000	$\sim 8 \times 10^{-4}$	0.6 \times 3.0	Rotation camera
7-3	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 \times 20.0	
Undulator Lines-VUV/soft X-ray							
5-2	1.5		Rowland circle-multiple grating	10 to 1,200	$\geq 7\%$ (raw undulator)	6.0 \times 8.0	Angle integrated e-spectrometer
Undulator Lines-X-ray							
PEP 1B							
Focused	1.7	22	Double crystal	12,000 to 22,000	2×10^{-5}	.5 \times 3	
Unfocused	Full		Double crystal	12,000 to 42,000	$\sim 10^{-5}$	0.6 \times 6.0	Six-circle diffractometer
PEP 5B							
Focused	1.7	22	Double crystal	12,000 to 22,000	2×10^{-5}	.5 \times 3	
Unfocused	Full		Double crystal	12,000 to 20,000	$\sim 10^{-5}$	0.6 \times 6.0	

CHARACTERISTICS OF SSRL EXPERIMENTAL STATIONS* (Continued)

	Horizontal angular acceptance, Mrad	Mirror cutoff, keV	Monochromator	Energy range, eV	Resolution $\Delta E/E$	Approximate spot size, hgt \times wtdh, mm	Dedicated instrumentation
Bending Magnet Stations							
X-ray							
1-4	2.0		Curved crystal	6,700 to 10,800	0.3×10^{-3}	0.25×0.5	Small angle scattering detector
1-5	1.0		Double crystal	2,800 to 30,000	$\sim 10^{-4}$	3×20	Area detector/CAD-4
2-1 (focused)	4.8	8.9	Double crystal	2,800 to 8,900	$\sim 5 \times 10^{-4}$	1×4	
2-2	1.0 to 6.1		None	3,200 to 30,000		4×22 to 4×134	
2-3	1.0		Double crystal	2,800 to 30,000	$\sim 5 \times 10^{-4}$	3×20	
VUV/soft X-ray							
1-1	2.0		Grasshopper	64 to 1,000	$\Delta\lambda = 0.1$ to 0.2 \AA	1.0×1.0	
1-2	4.0		6m TGM	8 to 90	$\sim 2 \times 10^{-3}$	1.0×2.0	
3-1	2.0		Grasshopper	25 to 1,000	$\Delta\lambda = 0.05$ to 2 \AA	1.0×1.0	
3-2	4.0		Seya-Namioka	5 to 40	$\Delta\lambda = 0.2$ to 6 \AA	2×7	
3-3	8 to 10	4.5	UHV double crystal (jumbo)	800 to 4,500	$\sim 5 \times 10^{-4}$	1.5×2.5	
3-4	0.6		Multilayer	0 to 3,000	White or $\Delta\lambda/\lambda = 0.6\%$	2×8	Vacuum diffractometer/ lithography exposure station
8-1	12		6m TGM	8 to 180	$\sim 9 \times 10^{-3}$	$\leq 1 \text{ mm}^2$	Angle resolved e-spectrometer
8-2	5		6m SGM	50 to 1,000	$E/\Delta E \leq 22,000$	$\leq 1 \text{ mm}^2$	Angle resolved e-spectrometer

*SSRL presently has 25 experimental stations, 23 of which are located on SPEAR and two on PEP. Eleven of these stations are based on insertion devices while the remainder use bending magnet radiation.

FY 1991 EQUIPMENT FUNDS

Outlay funds of the Office of Basic Energy Sciences are divided among operating, equipment, and construction funds. Equipment funds are provided primarily to DOE laboratories. (Operating funds provided to other contractors are used for all costs, including purchase of necessary equipment.) FY 1991 equipment funds for Chemical Sciences programs were assigned as follows:

Facility	Equipment funds	Facility	Equipment funds
Ames Laboratory	\$ 460,000	Los Alamos National Laboratory	50,000
Argonne National Laboratory	3,750,000	Notre Dame Radiation Laboratory	265,000
Brookhaven National Laboratory	1,730,000	Oak Ridge National Laboratory	2,179,000
Idaho National Engineering Laboratory	20,000	Pacific Northwest Laboratories	3,000,000
Lawrence Berkeley Laboratory	1,160,000	Sandia National Laboratories, Albuquerque	15,000
		Sandia National Laboratories, Livermore	880,000
		Solar Energy Research Institute	115,000
		Stanford Synchrotron Radiation Laboratory	700,000

SELECTED TOPICS OF GENERAL INTEREST

ACTINIDE CHEMISTRY

108, 114, 115, 116, 117, 118, 119, 120, 378, 379, 380, 381, 382

ANALYSIS

Mass Spectroscopy

92, 96, 99, 101, 102, 103, 104, 105, 110, 113, 343, 345, 346, 358, 361, 370, 408

Optical Spectroscopy

92, 94, 97, 98, 100, 104, 111, 338, 341, 342, 343, 344, 345, 347, 351, 352, 355, 364, 369, 374, 376, 377, 406

Miscellaneous

91, 93, 97, 103, 357, 359, 364, 368, 372

ATOMIC PHYSICS

Collisions

56, 58, 60, 61, 62, 63, 232, 237, 239, 249, 252, 255, 256

Fusion

37, 56, 58, 60, 61, 62, 232, 234, 237, 241, 251, 254, 255

Spectroscopy

39, 53, 54, 55, 230, 233, 238, 242, 243, 245, 247, 248, 250, 251, 254

Theory

59, 228, 229, 231, 235, 236, 237, 240, 241, 244, 246, 253

BIOSCIENCES (CHEMICAL)

84

CATALYSIS

Heterogeneous

30, 34, 66, 67, 68, 76, 79, 84, 257, 265, 267, 268, 269, 277, 278, 283, 284, 285, 288, 290, 291, 292, 296, 300, 304, 314, 315, 318, 319, 320, 322, 327, 328, 330, 331, 332

Homogeneous

12, 70, 76, 80, 90, 291, 303, 306, 308, 309, 329, 333, 334

Organometallic Chemistry (Carbon Monoxide Related)

12, 90, 261, 289, 303, 316, 329

Organometallic Chemistry (General)

64, 65, 70, 77, 80, 82, 258, 259, 263, 264, 270, 272, 275, 276, 280, 282, 286, 293, 294, 295, 297, 298, 306, 307, 308, 309, 311, 317, 323, 334

Surface Chemistry

76, 79, 87, 211, 217, 260, 266, 268, 281, 284, 296, 300, 304, 305, 310, 312, 315, 318, 320, 321, 325, 326

CHEMICAL ENERGY (MISCELLANEOUS)

78, 83, 262

COMBUSTION

Dynamics

31, 35, 38, 42, 140, 174, 177, 181, 182, 183, 185, 188, 194, 198, 202, 209, 210, 218, 219, 221, 222, 223, 225, 227

Kinetics

35, 36, 42, 50, 52, 173, 178, 187, 193, 194, 197, 199, 201, 204, 207, 213, 214, 215, 216, 218, 220, 224, 285

Spectroscopy and Analysis

33, 38, 42, 48, 49, 51, 174, 180, 181, 184, 187, 191, 192, 196, 198, 206, 209, 216, 219, 220, 221, 224, 285, 406, 408

Theory and Modeling

32, 35, 38, 40, 42, 45, 50, 51, 179, 186, 189, 195, 199, 203, 212, 213

Turbulence

121, 124, 383, 389, 405

ENVIRONMENTAL CHEMISTRY

17, 46, 47, 81, 88, 134, 226

FOSSIL CHEMISTRY

64, 69, 71, 72, 73, 77, 85, 89, 273, 274, 279, 287, 299, 313, 324

HOT ATOM CHEMISTRY

14, 134, 140, 183

MATERIALS PRECURSOR CHEMISTRY

70, 271, 282, 301, 302

PHOTOELECTRON SPECTROSCOPY

33, 39, 44, 176, 180, 208, 226

RADIATION CHEMISTRY

5, 8, 13, 18, 19, 21, 23, 25, 26, 142, 147, 148, 154, 167

SEPARATIONS

Chromatography

91, 94, 346, 347, 354, 356, 357, 368, 369, 372

Extraction

95, 109, 336, 339, 349, 363, 371, 379

Isotopes

340

Membranes

337, 350, 353, 360, 362, 365, 373, 407

Miscellaneous

106, 107, 112, 348, 366, 367, 375, 384, 404

SOLAR PHOTOCHEMICAL ENERGY CONVERSION

Electron Transfer Rates and Mechanisms

1, 2, 5, 9, 12, 13, 25, 125, 127, 129, 130, 131, 133, 139, 142, 146, 148, 149, 151, 152, 155, 163, 164, 165, 169

Initial Charge Separation in Natural Photosynthesis

3, 6, 7, 10, 27, 126, 135, 139, 159

Inorganic and Organometallic Photochemistry and Photophysics

12, 15, 20, 25, 129, 136, 137, 144, 149, 150, 151, 153, 159, 160, 171, 172

Microheterogeneous Systems

1, 5, 15, 22, 24, 27, 28, 29, 128, 130, 139, 143, 144, 146, 148, 149, 152, 153, 157, 165, 166, 167, 169, 170

Molecular Models

9, 10, 27, 127, 131, 137, 145, 164, 169, 171

Organic Photochemistry and Photophysics

18, 24, 25, 127, 130, 131, 139, 162, 164, 167, 168, 170

Photoelectrochemistry

11, 16, 22, 28, 29, 127, 132, 138, 139, 141, 145, 151, 156, 158, 161, 166, 167, 168, 169

SURFACE AND INTERFACIAL SCIENCE

30, 34, 37, 41, 44, 46, 47, 93, 141, 158, 175, 190, 200, 205, 211, 341, 359, 368, 377

SYNCHROTRON-RELATED PROJECTS

10, 12, 13, 36, 38, 39, 44, 76, 97, 288, 331

THERMODYNAMIC PROPERTIES AND PHASE EQUILIBRIA

31, 33, 43, 74, 75, 86, 119, 122, 123, 192, 207, 208, 335, 381, 384, 385, 386, 387, 388, 390, 391, 392, 393, 394, 395, 396, 397, 398, 399, 400, 402, 403

INSTITUTION INDEX

This index lists the institutions responsible for the projects cited in this publication. The corporate names are entered in standardized forms found in the authority listing *International Energy Research Organizations* (ETDE/PUB-3). Each entry includes the project title and citation number.

- Aerospace Corporation**
173
- Akron, University of**
125, 174
- Alabama, University of**
126
- Ames Laboratory, Iowa State University**
1, 2, 3, 4, 30, 31, 32, 64, 65, 66, 67, 68, 69, 91, 92, 93, 94
- Argonne National Laboratory**
5, 6, 7, 8, 9, 33, 34, 35, 53, 54, 55, 70, 71, 72, 73, 95, 96, 114
- Arizona State University**
127, 175
- Arizona, University of**
128, 176
- Auburn University**
257, 336
- Boston University**
129, 130
- Brandeis University**
131
- Brigham Young University**
337
- Brookhaven National Laboratory**
10, 11, 12, 13, 14, 36, 37, 38, 39, 56, 74, 75, 76, 97, 98
- Brown University**
338
- California Institute of Technology**
132, 258
- California State University, Fullerton**
228
- California, University of, Berkeley**
133
- California, University of, Irvine**
134, 259
- California, University of, Los Angeles**
135, 177, 339
- California, University of, San Diego**
383
- California, University of, Santa Barbara**
136, 260, 261
- Catholic University of America**
178
- Chicago, University of**
179
- Chromex, Inc.**
406
- Clark Atlanta University**
229
- Clarkson University**
384
- Clemson University**
137
- Colorado State University**
262, 263, 385
- Colorado, University of**
138, 180, 181, 230, 231, 264
- Columbia University**
139, 140, 141, 182, 183, 340
- Connecticut, University of**
265
- Cornell University**
184, 185, 232, 386, 387, 388, 389
- Dartmouth College**
142
- Delaware, University of**
266, 267, 341, 390
- Duke University**
342
- Emory University**
186, 187
- Florida State University**
378
- Florida, University of**
343, 344
- George Washington University, The**
345
- Georgia Institute of Technology**
188, 233, 234, 346
- Georgia, University of**
189, 190
- Hampton University**
347
- Harvard University**
191, 192, 235, 268
- Houston, University of**
143, 348
- Idaho National Engineering Laboratory**
99
- Idaho, University of**
349
- Illinois, University of, at Chicago**
193, 194, 391
- Illinois, University of, at Urbana-Champaign**
269, 270, 350, 351
- Indiana University**
271, 272, 273, 274
- Iowa, University of**
275
- Johns Hopkins University**
195, 392
- Kansas State University**
236, 237, 352
- Kentucky, University of**
196, 276
- Lawrence Berkeley Laboratory, University of California**
15, 16, 17, 40, 41, 42, 43, 44, 57, 58, 77, 78, 79, 80, 81, 82, 100, 115, 116, 121, 122
- Lawrence Livermore National Laboratory, University of California**
45
- Lehigh University**
277, 278, 353
- Los Alamos National Laboratory, University of California**
83, 117, 118, 119, 123
- Louisiana State University**
279
- Louisville, University of**
238, 280
- Marquette University**
144
- Maryland, University of**
393
- Massachusetts Institute of Technology**
145, 197, 198, 281, 282

- Massachusetts, University of, at Amherst
199, 200, 283, 394
- Massachusetts, University of, at Boston
146
- Membrane Technology & Research, Inc.
407
- Michigan State University
354
- Michigan, University of
201, 284, 355
- Minnesota, University of
147, 202, 203, 285, 356
- Missouri, University of, at Columbia
286
- Missouri, University of, at Rolla
357
- National Institute for Petroleum and Energy Research
395
- National Institute of Standards and Technology, Boulder
396
- National Institute of Standards and Technology, Gaithersburg
148, 204, 205, 206, 239, 358
- Nebraska, University of
240
- Nevada, University of
241, 287
- New Mexico, University of
242, 288, 379
- New Orleans, University of
207
- North Carolina State University
397
- North Carolina, University of, at Chapel Hill
149, 208, 289, 359
- North Carolina, University of, at Charlotte
150
- Northwestern University
151, 290, 291, 292, 293
- Notre Dame Radiation Laboratory, University of Notre Dame
18, 19, 20, 21, 22, 23, 24, 25, 26
- Oak Ridge National Laboratory
59, 60, 61, 62, 84, 85, 86, 87, 88, 101, 102, 103, 104, 105, 106, 107, 108, 109, 120
- Ohio State University
152, 380
- Oklahoma, University of
294, 360
- Oregon Graduate Institute of Science and Technology
153
- Oregon, University of
243, 295
- Pacific Northwest Laboratory
46, 47, 89, 110, 111, 112, 113
- Pennsylvania State University, Lehman
244
- Pennsylvania State University, University Park
154, 155, 296, 297, 298, 299
- Pennsylvania, University of
209, 210, 300, 301, 302, 303, 398
- Pittsburgh, University of
156, 211, 245, 304, 305
- Portland State University
157
- Princeton University
158, 159, 212, 213, 214, 399
- Purdue University
306, 361, 400
- Rensselaer Polytechnic Institute
215, 307, 362, 363
- Rice University
216, 217, 246
- Rochester, University of
160, 161, 162, 218, 219, 247, 308
- Rutgers University
163, 309, 310
- SRI International
220, 381
- Sandia National Laboratories, Albuquerque
63
- Sandia National Laboratories, Livermore
48, 49, 50, 51, 52, 124
- Solar Energy Research Institute
27, 28, 29, 90
- South Carolina, University of
311
- South Florida, University of
164
- Southern California, University of
221, 222, 223, 312
- Southern Illinois University
313
- Southwest Sciences, Inc.
408
- Stanford University
165, 224, 314, 315, 401
- State University of New York at Binghamton
316
- State University of New York at Buffalo
225, 317, 364
- State University of New York at Stony Brook
226, 402
- Syracuse University
166, 365, 366
- Tennessee, University of
167, 248, 367, 368, 369, 382
- Texas A & M University
249, 318, 319, 370
- Texas Tech University
371, 372
- Texas, University of, at Austin
168, 169, 170, 250, 320, 321, 373
- Toledo, University of
251, 252
- Tulane University
322
- Utah, University of
323, 324, 374, 375
- Vanderbilt University
253
- Virginia Commonwealth University
376
- Virginia Polytechnic Institute and State University
325
- Virginia, University of
254, 403
- Washington State University
171
- Washington, University of
326
- Wayne State University
172, 327
- Western Michigan University
255
- William and Mary, The College of
256
- Wisconsin, University of, at Madison
227, 328, 329, 404
- Wisconsin, University of, at Milwaukee
330
- Wyoming, University of
377
- Yale University
331, 332, 333, 334, 335, 405

INVESTIGATOR INDEX

Investigators' surnames are indexed in the form appearing in the citation; given names generally have been reduced to initials. For projects with multiple investigators, each name is indexed. Accent marks are not input because of computer alphabetization. Spelling and transliteration follow standard conventions.

- Adams, R.D., 311
Alexandratos, S.D., 367
Alnajjar, M.S., 89
Alston, S.G., 244
Andrews, M., 76
Angelici, R.J., 64
Appelhans, A.D., 99
Appelman, E.H., 114
Aris, R., 356
Armstrong, D.W., 357
Ashurst, W., 124
Athayde, A.L., 407
Atwood, J.D., 317
Autrey, S.T., 89
Baer, D.R., 110
Baer, T., 208
Baker, T.K., 257
Balasubramanian, K., 175
Barker, J.R., 201
Barkigia, K.M., 10
Barlow, R.S., 51
Barr, P.K., 124
Bartean, M.A., 266
Bartels, D.M., 8
Bartlett, N., 78
Bartsch, R.A., 371
Basaran, O.A., 106
Bausch, M., 313
Bayfield, J.E., 245
Beaudet, R.A., 221
Bein, T., 288
Beitz, J.V., 114
Belfort, G., 362
Bell, A.T., 79
Bentley, J., 19
Bercaw, J.E., 258
Bergman, R.G., 80
Berkowitz, J., 33
Bernstein, E.M., 255
Berry, D.H., 301
Berry, H.G., 53
Bersohn, R., 182
Beuhler, R.J., 37
Bielski, B.H.J., 13
Bloomquist, C.A.A., 73
Bocarsly, A.B., 158
Bohn, P.W., 350
Bomse, D.S., 408
Bottcher, C., 59
Botto, R.E., 73
Boudart, M., 314
Bowman, C.T., 224
Bowman, J.M., 186
Bowman, M.K., 6-7
Braun, C.L., 142
Brenner, A., 327
Brezinsky, K., 214
Bright, F.V., 364
Britt, P.F., 85
Brown, N.J., 40
Browner, R.F., 346
Brunschwig, B.S., 12
Bryant, H.C., 242
Buchanan, A.C., 85
Bullock, R.M., 76
Burns, C.J., 83, 118
Burns, J.H., 109
Bursten, B.E., 380
Byers, C.H., 106-107
Cabelli, D.E., 13
Calvin, M., 15
Campbell, C.T., 326
Cannon, B.D., 111
Carleson, T.E., 349
Carmichael, I.C., 19, 25
Carnall, W.T., 114
Carr, R.W., 356
Carrado, K.A., 73
Casey, C.P., 329
Caulton, K.C., 271
Cavanagh, R.R., 205
Ceyer, S.T., 281
Champion, R.L., 256
Chandler, D., 133
Chandler, D.W., 52
Chao, K.-C., 400
Chateaufneuf, J.E., 18
Chen, J.-Y., 51
Chen, J.H., 51
Chen, M.J., 70
Chen, P., 192
Cheng, R.K., 121
Chipman, D.M., 19
Chisholm, M.H., 272
Choppin, G.R., 378
Christian, S.D., 360
Christie, W.H., 101
Christou, G., 273
Clouthier, D.J., 196
Cochran, H.D., 107
Cohen, N., 173
Colson, S.D., 46
Connick, R.E., 81
Connolly, J.S., 27
Cool, T.A., 184
Cotton, T.M., 1
Cox, D.F., 325
Crabtree, R.H., 333
Cram, D.J., 339
Creutz, C., 12
Crim, F.F., 227
Crosby, G.A., 171
Crosley, D.R., 220
Cummings, P.T., 403
Curl, R.F., Jr., 216
Curtis, C.J., 90
Curtis, L.J., 251
Cutler, A.R., 307
D'Silva, A.P., 92
Dahl, D.A., 99
Dai, H.-L., 209
Dale, J.M., 103
Dalgarno, A., 235
Dasgupta, P.K., 372
Datz, S., 60
Davis, M., 35
Debenedetti, P.G., 399
Delmore, J.E., 99
DePristo, A.E., 30
Diebold, G.J., 338
DiMauro, L., 39
Dittner, P.F., 60-61
Donohue, M.D., 392
Doverspike, L.D., 256
Dryer, F.L., 213
DuBois, D.L., 90
DuBois, M.R., 264
Dumesic, J.A., 328
Duncan, M., 190
Dunford, R.W., 53
Dunning, T.H., Jr., 47
Durant, J.L., 50, 52
Dutta, P.K., 152
Dyrkacz, G.R., 73
Eberly, J.H., 247
Edelstein, N.M., 115
Egan, J.J., 74
Eischens, R.P., 277
Eisenberg, R., 160
Ekerdt, J.G., 320
El-Sayed, M.A., 135
Elliott, C.M., 262
Ellison, G.B., 180
Ely, J.F., 396
Endicott, J.F., 172
Erpenbeck, J.J., 123
Espenson, J.H., 65
Evans, W.J., 259
Eyring, E.M., 374
Fajer, J., 10
Farrar, J.M., 218
Farrow, R.L., 48
Fateley, W.G., 352
Fayer, M.D., 165
Feagin, J.M., 228
Feldberg, S.W., 11
Felker, P.M., 177
Fendler, J.H., 166
Feraudi, G.J., 20
Ferrieri, R.A., 14
Fessenden, R.W., 21
Field, R.W., 198
Finke, R.G., 295
Fischer, C.F., 253
Fish, R.H., 77
Fisk, G.A., 50, 52
Flynn, G.W., 183
Fontijn, A., 215
Ford, P.C., 261
Fox, M.A., 168
Frank, A.J., 28
Franz, J.A., 89
Frei, H., 16
Freiser, B.S., 361
Friedlander, G., 37
Friedman, L., 37

- Friend, C.M., 268
Friesner, R.A., 139
Fripiat, J., 330
Fritz, J.S., 91
Fujita, E., 12
Fulton, J.L., 112
Fung, K.H., 98
Gajewski, J.J., 274
Gallagher, T.F., 254
Gates, B.C., 267
Gentry, W.R., 202
Geoffroy, G.L., 297
Gerardo, J.B., 63
Gerstein, B.C., 66
Gibson, D.H., 280
Gibson, J.K., 120
Giese, C.F., 202
Gladysz, J.A., 323
Gland, J.L., 284
Glandt, E.D., 398
Glass, G.P., 216
Glassman, I., 214
Glish, G.L., 102
Gobeli, G.W., 406
Goeringer, D.E., 102
Goldman, A.S., 309
Goldsmith, J.E., 49
Gonzalez, R.D., 322
Goodman, D.W., 318
Gordon, B.M., 97
Gordon, R.J., 194
Gorte, R.J., 300
Gottlieb, C., 191
Gould, H.A., 57
Graff, M.M., 188
Grant, B.C., 103
Grant, D.M., 324
Gray, S., 35
Greenbaum, E., 84
Greenberg, K.E., 63
Greene, C.H., 231
Grover, J.R., 39
Gubbins, K.E., 386
Guiochon, G., 368
Gust, J.D., Jr., 127
Gutman, D., 178
Hagaman, E.W., 85
Haire, R.G., 120
Hall, C.K., 397
Hall, G.E., 38
Haller, G.L., 332
Hanson, R.K., 224
Harding, L., 35
Hargis, P.J., 63
Harold, M.P., 283
Harris, C.B., 41
Harrison, R., 35
Harrison, W., 343
Havener, C.C., 62
Hayatsu, R., 73
Hayden, C.C., 52
Heinekey, D.M., 334
Helman, W.P., 25
Henrich, V., 331
Hercules, D.M., 304
Herman, R.G., 278
Herron, J.T., 204
Hessler, J., 35
Hildenbrand, D.L., 381
Ho, P.C., 86
Hobart, D.E., 117
Hoffman, D.C., 116
Hoffman, M.Z., 129
Holmes, H.F., 86
Holroyd, R.A., 13
Homsy, G.M., 401
Horwitz, E.P., 95
Hougen, J.T., 206
Houk, R.S., 92
Houston, P.L., 185
Howard, J.B., 197
Hrbek, J., 76
Hubbard, C.W., 110
Hug, G.L., 18, 25
Hulett, L.D., 103
Hunt, J.E., 96
Huntley, D.R., 87
Hupp, J.T., 151
Hurst, J.K., 153
Hurtubise, R.J., 377
Isied, S.S., 163
Jackson, B.E., 200
Janda, K.C., 211
Jellinek, J., 34
Johnson, B.M., 56
Johnson, E., 120
Johnson, J.R., 75
Johnson, P.M., 226
Johnston, H.S., 17
Jonah, C.D., 8
Jones, G., 130
Jones, K.W., 97
Jones, W.D., 308
Jordan, R.F., 275
Kamat, P.V., 22
Kanter, E.P., 54
Kee, R.J., 50
Kelley, M.H., 239
Kern, R.D., Jr., 207
Kerstein, A.R., 124
Keto, J.W., 250
Kevan, L., 143
Kiefer, J.H., 193
Kielkopf, J., 238
Kincaid, J.R., 144
King, D.S., 205
King, T.S., 67
Kispert, L.D., 126
Kleinschmidt, P.D., 119
Klemm, R.B., 36
Klier, K., 278
Klingler, R.J., 70
Knickerbein, M.B., 34
Koel, B.E., 312
Koetzle, T.F., 76
Koros, W., 373
Kostic, N.M., 2
Kostroun, V.O., 232
Koszykowski, M.L., 49
Koval, C.A., 138
Krause, H.F., 60
Krause, M.O., 87, 120
Kubas, G.J., 83
Kung, A.H., 42
Kung, H.H., 290
Kvale, T.J., 252
Kwok, H.-S., 225
Lamb, J.D., 337
Lampe, F.W., 154
Lane, N.F., 246
Lau, K.H., 381
LaVerne, J.A., 23
Lee, Y.T., 42
Lees, A.J., 316
Lenz, T.G., 385
Leone, S.R., 181
Lester, M.I., 210
Lester, W.A., 42
Lewis, N.S., 132
Libby, P.A., 383
Lichtenberger, D.L., 176
Light, J.C., 179
Lim, E.C., 125
Lin, C.D., 236
Lin, M.-C., 187
Lin, Y., 8
Linehan, J.C., 89
Linschitz, H., 131
Lipsky, S., 147
Liu, K., 35
Long, M.B., 405
Lucht, R.P., 48-49
Lucia, A., 384
Lunsford, J.H., 319
MacDonald, R., 35
Madden, K.P., 21
Madey, T.E., 310
Madix, R.J., 315
Mallouk, T.E., 169
Marks, T.J., 291
Maroncelli, M., 155
Masel, R.I., 269
McBeth, R.L., 73
McClelland, J.J., 239
McGown, L.B., 342
McGuffin, V.L., 354
McLuckey, S.A., 102
McMahon, J.M., 105
McMullan, R.K., 76
Meisel, D., 5
Melnicoff, P.E., 73
Mesmer, R.E., 86
Meyer, F.W., 62
Meyer, T.J., 149
Meyerhofer, D.D., 247
Michael, J., 35
Miller, A.C., 278
Miller, J.A., 50, 52
Miller, J.D., 375
Miller, J.R., 5
Miller, R.J., 111
Miller, R.J.D., 161
Miller, W.H., 42
Monson, P.A., 394
Montaser, A., 345
Moore, A.L., 127
Moore, C.B., 42
Moore, T.A., 127
Morris, M.D., 355
Morss, L.R., 114
Moyer, B.A., 109, 120
Mozumder, A., 23
Msezane, A.Z., 229
Muckerman, J.T., 38
Mullins, D.R., 87
Murad, S., 391
Murray, R.W., 359
Neta, P., 148
Neuman, R.D., 336
Neumark, D., 42
Newton, M., 12
Ng, C.Y., 31
Nicholas, K.M., 294
Norris, J.R., 6-7
Norton, J.R., 263
Nozik, A.J., 29
O'Connell, J.P., 403
Osgood, R.M., Jr., 141
Otvos, J.W., 15
Overbury, S.H., 87
Pagni, R.M., 88
Paine, R.T., 379

- Painter, P.C., 299
Palmer, D.A., 86
Panagiotopoulos, A.Z., 387
Parks, E.K., 34
Patterson, L.K., 24, 26
Paul, D., 373
Paul, P.H., 51
Pegg, D.J., 248
Perry, D.S., 174
Petersen, J.D., 137
Peterson, J.R., 120, 382
Phaneuf, R.A., 62
Pimblott, S., 23
Pitzer, K.S., 43
Pope, S.B., 389
Porter, M.D., 93
Potts, K.T., 363
Prausnitz, J.M., 122
Preses, J., 38
Prior, M.H., 58
Pugmire, R.J., 324
Rabideau, P.W., 279
Rabitz, H.A., 212
Rahn, L.A., 48
Rakestraw, D.J., 49
Ramsey, J.M., 104
Rathke, J.W., 70
Rauchfuss, T.B., 270
Raymer, M.G., 243
Regen, S.L., 353
Reilly, J.J., 75
Reisler, H., 222
Renner, M.W., 10
Richard, P., 237
Riley, S.J., 34
Rillema, D.P., 150
Rizzo, T.R., 219
Rohlfing, E.A., 52
Ross, A.B., 25
Rosseel, T.M., 101
Rowland, F.S., 134
Roy, R., 233
Ruedenberg, K., 32
Russell, D.H., 370
Russo, R.E., 100
Rutan, S.C., 376
Sachleben, R.A., 109
Sachtler, W.M.H., 292
Sandler, S.I., 390
Sattelberger, A.P., 118
Sauer, M.C., Jr., 8
Scamehorn, J.F., 360
Schaefer, H.F., III, 189
Scheeline, A., 351
Schefer, R.W., 51
Schmidt, L.D., 285
Schrader, G.L., 68
Schrock, R.R., 282
Schuler, R.H., 23, 26
Schwarz, H.A., 13
Scott, L.T., 287
Scott, T.C., 106
Sears, T.J., 38
Seibert, M., 27
Selegue, J.P., 276
Seltzer, S., 12
Sen, A., 298
Sengers, J.V., 393
Sepaniak, M.J., 369
Sharp, P.R., 286
Shaw, R.W., 104
Shepard, R., 35
Shirley, D.A., 44
Shriver, D.F., 293
Sieck, L.W., 358
Sigman, M.E., 88
Silbey, R., 198
Simmons, G.W., 278
Simonson, J.M., 86
Small, G.J., 3
Smalley, J.F., 11
Smalley, R.E., 217
Smith, D.H., 105
Smith, R.D., 112
Smith, S.J., 230
Smooke, M.D., 405
Sneddon, L.G., 302
Soderholm, L., 114
Spiro, T.G., 159
Squires, R.R., 306
Starace, A.F., 240
Steele, W.V., 395
Stell, G.R., 402
Stern, S.A., 365
Stevens, B., 164
Stewart, W.E., 404
Stock, L.M., 71
Struve, W.S., 4
Styris, D.L., 110, 113
Suib, S.L., 265
Sullivan, J.C., 114
Sutherland, J.W., 36
Sutin, N., 12
Sweeney, D.W., 51
Talbot, L., 121
Tang, I.N., 98
Tang, J., 7
Tanis, J.A., 255
Templeton, J.L., 289
Thaddeus, P., 191
Thomas, E.W., 234
Thompson, M.A., 10
Thurnauer, M., 7
Tiede, D.M., 6-7
Tien, C., 366
Tiller, F.M., 348
Todd, P.J., 101
Tollin, G., 128
Toth, L.M., 108
Trahanovsky, W.S., 69
Trebino, F.P., 49
Trifunac, A.D., 8
Tripathi, G.N.R., 26
Truhlar, D., 203
Tully, F.P., 52
Turner, J.A., 29
Turro, N.J., 340
Urasa, I.T., 347
Valentini, J.J., 140
Van Berkel, G.J., 102, 105
van Willigen, H., 146
Vane, C.R., 60
Vannice, M.A., 296
Vaughan, J.D., 385
Vollhardt, K.P.C., 82
Vorres, K.S., 72
Wagner, A., 35
Waldeck, D.H., 156
Wamser, C.C., 157
Wasielewski, M.R., 7, 9
Watson, R.L., 249
Watts, R.J., 136
Wayland, B.B., 303
Webber, S.E., 170
Weinberg, W.H., 260
Werst, D.W., 8
Westbrook, C.K., 45
Westmoreland, P.R., 199
Weston, R.E., 38
White, J.M., 321
White, M., 39
Whitten, D.G., 162
Whitten, W.B., 104
Wiberg, K.B., 335
Williams, T.F., 167
Winans, R.E., 73
Winefordner, J.D., 344
Winkler, P., 241
Winter, T.G., 244
Wirth, M.J., 341
Wishart, J.F., 13
Wittig, C., 223
Wolf, A.P., 14
Woodward, J., 84
Wrighton, M.S., 145
Yarkony, D.R., 195
Yates, J.T., Jr., 305
Yeung, E.S., 94
Yonker, C.R., 112
Young, J.P., 104
Young, L., 55
Zingg, S.P., 88
Zollweg, J.A., 388

