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Summaries of FY 1988 Research in the Chemical Sciences

September 1988

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

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

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 six 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 energy technologies can evolve. As a result, scientific excellence is a major criterion applied to 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.

For the first time, a separate section of this publication includes summaries of projects funded during FY 1988 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

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*On leave from Seton Hall University.

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

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 electricity 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. A growing program of photochemistry, spectroscopy, and related studies is centered at the National Synchrotron Light Source at Brookhaven National Laboratory.

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 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 most 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 constitute 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 Isotopes Reactor (HFIR) at Oak Ridge, 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 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 summary.

In addition, two facilities at Oak Ridge are operated as a service to the scientific community: the Transuranium Processing Plant (TPP) and the Electromagnetic Isotopes Enrichment Facility (Calutrons).

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, bio-, inorganic, physical, thermo-, and electrochemistry are central to these programs. The emphasis is on understanding the 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 is directed toward improving our basic understanding of methods for separating mixtures of gases, liquids, solids, and their component molecules, cations, anions, and isotopes. 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 program is technique oriented rather than species oriented; i.e., the research involves elucidating fundamental chemical phenomena for improved separations rather than developing specific processes for the separation of a particular species from particular matrices. The isotope separation program emphasizes isotopic properties and isotope effects and is basic in nature.

The analysis part of the program is aimed at supporting research on analytical techniques where a better understanding of basic chemical phenomena may facilitate improvements in sensitivity, reliability, and ease of operation and/or lower the costs of analytical determinations. Entirely new analytical techniques are also investigated, although this program does not support instrument development. New techniques are quickly reported in the literature so that those

interested in instrument development can build on work supported herein. The program is not geared to using existing techniques to unravel the composition of samples nor to developing techniques to analyze particular chemical species or sample types. Rather, it is aimed at obtaining a thorough understanding of the basic chemistry of an analytical technique so that others may use this understanding to improve its utility.

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 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 actinides in complex oxides and binary halides, (4) the chemistry of actinides in near-neutral aqueous solutions and the reactions of aqueous actinides ions with various complexing agents, (5) the development of preparative methods for actinide metals and compounds, and (6) the measurement of crystal structures, melting points, magnetic susceptibilities and the behavior of actinide metals and compounds 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 the more specific and energy-related aspects of chemically related engineering topics, including thermodynamics and physical and chemical rate processes. Particular attention is given to turbulence research related to combustion, experimental and theoretical thermochemical and thermophysical properties, and phase equilibria, especially of mixtures, including supercritical phenomena. 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.

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Table of Contents

NATIONAL LABORATORIES			
Photochemical and Radiation Sciences			
Ames Laboratory	1	Boston University	32
Argonne National Laboratory	1	Bowling Green State University	32
Brookhaven National Laboratory	3	California, University of	32
Lawrence Berkeley Laboratory	4	California Institute of Technology	34
Notre Dame Radiation Laboratory	5	Clemson University	34
Solar Energy Research Institute	7	Colorado, University of	34
		Columbia University	35
Chemical Physics		Dartmouth College	35
Ames Laboratory	8	Houston, University of	35
Argonne National Laboratory	9	Louisiana State University	35
Brookhaven National Laboratory	9	Marquette University	35
Lawrence Berkeley Laboratory	11	Massachusetts, University of	36
Lawrence Livermore National Laboratory	12	Massachusetts Institute of Technology	36
Oak Ridge National Laboratory	12	Minnesota, University of	36
Sandia National Laboratories	12	National Bureau of Standards	36
		Nebraska, University of	37
Atomic Physics		North Carolina, University of	37
Argonne National Laboratory	14	North Carolina at Charlotte, University of	37
Brookhaven National Laboratory	15	Northwestern University	38
Lawrence Berkeley Laboratory	15	Oregon Graduate Center	38
Oak Ridge National Laboratory	15	Pennsylvania State University	38
Sandia National Laboratories	16	Princeton University	38
		Rochester, University of	39
Chemical Energy		South Florida, University of	39
Ames Laboratory	16	Stanford University	40
Argonne National Laboratory	17	Syracuse University	40
Brookhaven National Laboratory	18	Tennessee, University of	40
Lawrence Berkeley Laboratory	19	Texas, University of	40
Los Alamos National Laboratory	21	Washington State University	41
Oak Ridge National Laboratory	21	Washington University	41
Pacific Northwest Laboratory	22	Wayne State University	41
Sandia National Laboratories	22		
Solar Energy Research Institute	23	Chemical Physics	
		Aerospace Corporation	42
Separations and Analysis		Arizona, University of	42
Ames Laboratory	23	Arizona State University	42
Argonne National Laboratory	24	Brown University	42
Brookhaven National Laboratory	24	California, University of	43
Idaho National Engineering Laboratory	25	Chicago, University of	43
Monsanto Research Corporation-Mound	25	Colorado, University of	43
Oak Ridge National Laboratory	25	Columbia University	43
Pacific Northwest Laboratory	27	Cornell University	44
		Emory University	44
Heavy Element Chemistry		Georgia, University of	44
Argonne National Laboratory	28	Georgia Institute of Technology	45
Lawrence Berkeley Laboratory	28	Harvard University	45
Los Alamos National Laboratory	28	Howard University	45
Oak Ridge National Laboratory	29	Illinois, University of	45
		Illinois Institute of Technology	46
Chemical Engineering Sciences		Iowa, University of	46
Lawrence Berkeley Laboratory	29	Jackson State University	46
Los Alamos National Laboratory	30	Kentucky, University of	47
Sandia National Laboratories	30	Massachusetts, University of	47
		Massachusetts Institute of Technology	47
OFFSITE INSTITUTIONS		Michigan, University of	48
Photochemical and Radiation Sciences			
Alabama, University of	31		
Arizona, University of	31		
Arizona State University	31		

Minnesota, University of	48	Kentucky, University of	66
National Bureau of Standards	48	Lehigh University	67
New Orleans, University of	49	Louisiana State University	67
New York/Buffalo, State University of	49	Louisville Research Foundation, University of	67
New York/Stony Brook, State University of	49	Massachusetts, University of	67
North Carolina, University of	50	Massachusetts Institute of Technology	68
Pennsylvania, University of	50	Minnesota, University of	68
Pittsburgh, University of	50	Missouri, University of	68
Princeton University	50	National Bureau of Standards	68
Purdue University	51	Nevada, University of	69
Rensselaer Polytechnic Institute	51	New York/Buffalo, State University of	69
Rice University	52	North Carolina, University of	69
Rochester, University of	52	Northwestern University	69
Southern California, University of	52	Pennsylvania, University of	70
SRI International	53	Pennsylvania State University	71
Stanford University	53	Pittsburgh, University of	72
Wisconsin, University of	53	Purdue University	72
Atomic Physics		Rensselaer Polytechnic Institute	73
Atlanta University	54	Rochester, University of	73
California State University-Fullerton	54	South Carolina, University of	73
Colorado, University of	54	SRI International	73
Cornell University	54	Stanford University	74
Georgia Institute of Technology	55	Syracuse University	74
Harvard University	55	Texas, University of	74
Jackson State University	55	Texas A and M University	75
Kansas, University of	55	Utah, University of	75
Kansas State University	56	Wayne State University	76
Louisiana State University	56	Wisconsin, University of	76
Louisville, University of	56	Yale University	77
National Bureau of Standards	57	Separations and Analysis	
Nebraska, University of	57	Aerospace Corporation	78
New Mexico, University of	57	Auburn University	78
Pennsylvania State University	58	Brigham Young University	78
Pittsburgh, University of	58	Brown University	78
Purdue University	58	California, University of	79
Rice University	58	Columbia University	79
Rochester, University of	58	Delaware, University of	79
St. John Fisher College	59	Duke University	79
Tennessee, University of	59	Florida, University of	79
Texas, University of	59	George Washington University	80
Texas A and M University	59	Georgia Institute of Technology	80
Toledo, University of	59	Hampton University	80
Vanderbilt University	60	Houston, University of	80
Virginia, University of	60	Idaho, University of	81
Western Michigan University	60	Illinois, University of	81
William and Mary, The College of	60	Kansas State University	81
Chemical Energy		Lehigh University	81
Brigham Young University	61	Maryland, University of	81
California, University of	61	Minnesota, University of	82
California Institute of Technology	61	Missouri, University of	82
Chicago, University of	62	National Bureau of Standards	82
Colorado, University of	62	New York/Stony Brook, State University of	82
Colorado State University	63	North Carolina, University of	83
Connecticut, University of	63	Oklahoma, University of	83
Delaware, University of	64	Oklahoma State University	83
Harvard University	64	Purdue University	83
Illinois, University of	64	Rensselaer Polytechnic Institute	84
Indiana University	65	San Diego State University	84
Indiana University-Purdue University	66	Syracuse University	84
Iowa, University of	66		

Tennessee, University of	84	Louisiana State University	92
Texas, University of	85	Maryland, University of	92
Texas A and M University	85	Massachusetts Institute of Technology	93
Texas Tech University	86	National Bureau of Standards	93
Utah, University of	86	National Institute for Petroleum and Energy Research (NIPER)	93
Virginia, University of	87	New York/Stony Brook, State University of	93
Virginia Commonwealth University	87	Pennsylvania, University of	94
Wyoming, University of	87	Princeton University	94
Heavy Element Chemistry		Purdue University Research Foundation	94
Florida State University	87	Stanford University	94
New Mexico, University of	88	Virginia, University of	95
Ohio State University	88	Wisconsin, University of	95
SRI International	88	Yale University	95
Tennessee, University of	88	Small Business Innovation Research	
Chemical Engineering Sciences		Bend Research, Inc.	95
American University	89	Precision Analytics, Inc.	96
Brigham Young University	89	Spectral Sciences, Inc.	96
California, University of	89	Spire Corporation	96
California/San Diego, University of	90	Texas Research Institute	96
Clarkson University	90		
Colorado State University	90	SPECIAL FACILITIES	97
Cornell University	91	FY 1988 EQUIPMENT FUNDS	109
Delaware, University of	91	INSTITUTION INDEX	111
Florida, University of	91	SELECTED TOPICS OF GENERAL INTEREST	113
Illinois, University of	91	INVESTIGATOR INDEX	114
Johns Hopkins University	92		

SUMMARIES OF FY 1988 RESEARCH IN THE CHEMICAL SCIENCES

NATIONAL LABORATORIES

Photochemical and Radiation Sciences

Ames Laboratory
Iowa State University
Ames, Iowa 50011

1. Photoinduced Electron-Transfer Reactions in Protein Matrices
N.M. Kostić

Electron-transfer reactions are involved in photosynthesis and in other processes for the utilization of solar energy. This research concerns the rates and mechanisms of electron-transfer reactions involving metalloproteins. Selective attachment of inorganic chromophores and of redox-active organometallic complexes to cytochrome *c*, cross-linking of cytochrome *c* via a dirhodium complex, and cross-linking of cytochrome *c* to plastocyanin have yielded several new electron-transfer systems. These systems have been characterized chromatographically, spectroscopically, and electrochemically. Long-range electron-transfer reactions are being studied by stopped-flow spectrophotometry and by photolysis. Cytochrome *c* undergoes a photoinduced, ground-state electron-transfer reaction in which this protein apparently stores light energy and converts it into chemical energy. A covalent complex between cytochrome *c* and plastocyanin, a stable analog for the precursor complex between these two metalloproteins, permits the measurement of the rate of interprotein oxido-reduction. [2.7 FTE]

2. Laser Spectroscopy and Electronic Energy Transfer of Light Conversion Systems
G.J. Small

The project objective is to develop a firm understanding of the early time electronic excitation and electron-transfer events of photosynthesis. This understanding will depend on knowledge of protein-pigment structure and the static and dynamical roles of the protein in transport phenomena that occur on a picosecond or shorter time scale. Both state-of-the-art frequency and time domain laser optical spectroscopies are essential for providing the data required for elucidating the crucial link between structure and dynamics. Laser-based high-resolution line-narrowing spectroscopies, developed in this laboratory for biological applications, are being used to study excitation transport and electron transfer in photosynthetic antenna (light-harvesting) and reaction center protein complexes. The spec-

troscopies include spectral hole burning and fluorescence line narrowing. They are ideally suited for elucidating both the excited electronic state structures of photosynthetic pigment complexes and the transport dynamics (including the role of the protein). The novel data generated are used to test existing theoretical models and to develop new theories. Data obtained have provided new insights into the role of coherence and the protein in electronic excitation transport and the types of charge-transfer states that may be important for the initial charge separation step in the reaction center (photosynthetic bacteria). The resulting theoretical models are being tested experimentally. [2.5 FTE]

3. Picosecond Spectroscopy and Reaction Dynamics
W.S. Struve

Picosecond fluorescence and pump-probe spectroscopies are used to study electronic excitation transport (EET) in light-harvesting and core antenna complexes of green photosynthetic organisms. The principal issues being addressed are the random-walk versus excitonic nature of EET, the relationships between EET and chromophore architecture in structurally well-characterized complexes, and the possibility that mechanisms other than dipole-dipole coupling contribute to singlet EET. Systems currently studied include the bacteriochlorophyll *a*-protein complex from the sulfur bacterium *Prosthecochloris aestuarii* and the chlorophyll *a* core antenna complex in enriched P700 photosystem I particles; planned studies will deal with the chlorophyll *a/b* light-harvesting complex of photosystem II and with the light-harvesting complex of the purple bacterium *Rps. sphaeroides*. Electron-transfer kinetics on the surface of ultrasmall semiconductor colloidal particles and dispersive excitation transport for chlorophyll *a* molecules in low-temperature glasses between 10 and 300 K are also being examined. [2.2 FTE]

Argonne National Laboratory
Argonne, Illinois 60439

Chemistry Division

\$5,470,000

4. Electron Transfer and Energy Conversion
J.R. Miller, D. Meisel, K.H. Schmidt

Basic scientific principles underlying possible technologies in photochemical solar energy capture and storage and in

processing of nuclear wastes are examined using pulse radiolysis and laser photolysis. The effects of distance, energy, and molecular structure on rates of electron transfer between molecules are probed to learn fundamental principles that can be applied to producing efficient systems for capturing light energy by charge separation reactions. Techniques have been developed to hold two electron donor/acceptor molecules at a fixed, known distance by attaching them to spacer molecules. Enhancements in equipment and technique this year enable the measurement of electron-transfer rates with a time resolution of 150 ps. New measurements are indicating how the energy levels of the spacer group control electron-transfer rates. This information is needed to design charge separation systems and to understand an important natural charge separation system, the photosynthetic reaction center. Redox catalysis by colloidal particles of semiconductors has potential to promote efficient energy conversion, particularly for using sunlight to drive useful chemical reactions. The important steps are electron and proton transfer at the surfaces of the colloidal particles. The techniques allow insights into how these reactions may be promoted and controlled, and how they are affected by the electronic structure of the colloids, including quantum size effects on the energy band structures. Electron-transfer and hydrolysis reactions of d- and f-transition elements, particularly the actinides, are measured in environmentally important situations: aqueous solutions and also on colloidal particles in aqueous solutions. The colloidal particles, which are present in natural waters and are formed inadvertently in nuclear reprocessing, can have dominant effects on the mobility and chemistry of radioactive materials. [9.7 FTE]

5. **Physicochemical Investigation of Photosynthesis**
*J.R. Norris, M.K. Bowman, J. Tang,
M. Thurnauer, D.M. Tiede, M.R. Wasielewski*

The project objective is to understand the mechanism of the primary act of light conversion in bacterial and green plant reaction centers. The tools used in these studies include natural, isotopically substituted, and genetically engineered cells and their components; crystalline reaction centers; and advanced optical and magnetic resonance techniques. Bacterial photosynthesis has been explained in considerable detail through the study of crystalline bacterial reaction centers, and this work is being refined and extended to the green plant photosystems. Genetically engineered cells and new physical and theoretical techniques are combined to elucidate further the details of the bacterial reaction center. Green plant photosynthesis is being studied by electron paramagnetic resonance and ultrafast optical techniques with the assistance of fully deuterated cells. The ultimate objective of this project is to describe photosynthesis in detail sufficient to enable the laboratory construction of efficient artificial systems. [7.5 FTE]

6. **Chlorophyll and Photosynthesis Research**
J.R. Norris, T.J. Michalski

The project objective is to understand chlorophyll function at the molecular level in the light conversion events of photosynthesis. Emphasis is on fundamental chlorophyll chemistry, the self-assembly of chlorophyll, and the enzymatic synthesis of intermediates useful in the construction of model systems. Advantage is taken of the coordination behavior of chlorophylls to prepare laboratory systems that mimic *in vivo* antenna chlorophyll in order to provide an experimental foundation for an

understanding of antenna structure and function. Chlorophyll micelles are characterized by small-angle neutron scattering and electron paramagnetic resonance analysis. New methods for the preparation and study of bacteriochlorophylls *b* and *g* are being developed, especially with respect to the nature of bacteriochlorophyll binding in reaction center protein. Model systems studies emphasize the use of enzymatic synthesis to examine chlorophyllous intermediates unobtainable by more rigorous chemical means. [3.0 FTE]

7. **Preparation of Organisms, Photosynthetic Pigments, and Biological Materials of Unusual Isotopic Composition**
D.M. Tiede, J.R. Norris

Isotopically altered and genetically engineered whole cells and cell components are provided to enhance the utility of the spectroscopies used to study photosynthesis. The magnetic resonance techniques used in photosynthesis research often require isotopically substituted and natural abundance whole cells and cell components that can only be obtained by biosynthesis with algae, cyanobacteria, and photosynthetic bacteria. Fully deuterated algae are routinely mass cultured by autotrophic growth in heavy water containing 99.7 atom percent deuterium. These algae and cyanobacteria are a source of ^2H -chlorophyll and ^2H -carotenes and also provide the organic substrates necessary for the culture of ^2H photosynthetic bacteria. [1.3 FTE]

8. **Reactive Intermediates in Condensed Phases: Radiation and Photochemistry**
*A.D. Trifunac, C.D. Jonah, M.C. Sauer, Jr.,
D.M. Bartels, D.B. McDonald, K.H. Schmidt*

The interactions of ionizing radiation with matter are studied in this project, with particular emphasis on the chemical consequences of excess energy in molecular systems. These studies deal with the pathways by which highly excited molecules and excited radicals and ions dissipate their excess energy. These processes are important because they provide the mechanisms by which the kinetic energy of an ionizing particle is transformed into chemical potential energy. The excited states are also interesting because they are expected to be more similar to transition states than to the normal ground state of the molecules. Because the transformation of such highly excited states to lower energy states is expected to take place very quickly, very fast techniques are necessary to study them. The ultrafast phenomena are studied in real time using state-of-the-art tools to create the transients, including a high-current electron linac (whose pulse has been compressed to about 7 ps), a pulsed electron Van de Graaff accelerator, and a picosecond ultraviolet laser with kilohertz repetition rate and high power. Optical, conductivity, and magnetic resonance detection are used to study the transients and their reactions both in liquids and in solids. [16.0 FTE]

9. **Artificial Photosynthesis**
M.R. Wasielewski

The project objective is to construct molecular assemblages that will perform photosynthetic energy conversion in the laboratory. Work for this research will involve: (1) synthesizing molecules containing two or more electron and/or energy donors and acceptors to serve as models for the donor-acceptor molecules in reaction center proteins; (2) examining the photophysics and photochemistry of these molecules with primary emphasis on

light-induced energy and electron-transfer reactions; and (3) comparing closely the information that we derive from studies of these molecules with data obtained from investigations of natural photosynthesis. These comparative studies lead to a better understanding of both natural and model energy- and electron-transfer processes. Ultrafast spectroscopic techniques are developed and used to characterize the excited and ionic states of these artificial systems. [4.5 FTE]

Brookhaven National Laboratory
Upton, Long Island, New York 11973

Department of Applied Science **\$990,000**

10. Porphyrin Chemistry
J. Fajer

This project addresses the role of porphyrin derivatives in bioenergetic reactions with particular emphasis on the mechanisms by which light is harvested and converted into chemical energy in photosynthesis. The extensive body of structural, theoretical, and experimental data evolving from this work is equally applicable to electron-transfer mechanisms of the broad class of porphyrins in widely diverse chemical reactions. The work also exploits the chemistry of recently discovered iron, cobalt, and nickel hydrophorphyrins that mediate nitrogen assimilation, hydroxylations, and carbon dioxide conversion to methane. The project uses photochemistry, spectroelectrochemistry, magnetic resonance, x-ray and neutron diffraction, and synchrotron radiation techniques that are closely supported by several theoretical methods. For example, theoretical considerations have provided attractively simple explanations for the range of absorption maxima exhibited by photosynthetic bacteria and for the direction of electron flow in their reaction centers in terms of structural variations in the architecture and conformations of the chromophores that function as electron donors and acceptors. Similar considerations offered a rationale for the antenna systems of green photosynthetic bacteria. A combination of electronic and structural factors was shown to control the reactions of nickel hydrophorphyrins that lead to methane generation. The project combines theoretical, structural, and experimental techniques to characterize transients and mechanisms in biocatalytic conversions, and to provide specific guidelines for the development of synthetic photocatalytic systems. [6.7 FTE]

11. Electrochemistry and Photoelectrochemistry
S. Feldberg

The project objective is a fundamental understanding of a variety of electrochemical and photoelectrochemical phenomena. Areas of interest comprise a mixture of experimental and theoretical investigations and involve a number of collaborations outside Brookhaven National Laboratory. The major experimental effort addresses the development and application of a laser-induced-temperature-jump perturbation of interfacial electrode temperature, a new technique for investigating very fast heterogeneous (electrochemical) phenomena in the submicrosecond time domain. A variety of experimental systems are being examined involving heterogeneous electron transfer, ion adsorption/desorption, relaxation of the electrical double layer, and the response of electronically conducting polymer films. A parallel effort has developed the requisite theory for the analysis of these data. A theoretical effort to

explain apparent time-independent hysteresis often observed in the cyclic voltammetry of ion-intercalating systems in general (and electronically conducting polymers in particular) may play an important role in understanding the temperature-jump studies of polyaniline (an electronically conducting polymer). Computer simulation of a variety of electrochemical problems is a significant, continuing contribution. [3.6 FTE]

Chemistry Department **\$3,355,000**

12. Radiation Chemistry
*R.A. Holroyd, H.A. Schwarz, B.H.J. Bielski,
J. Wishart*

In order to understand and control chemical reactions, it is essential to know the properties of the transient species that are involved as intermediates in the reactions. For instance, various forms of iron(IV) have been postulated as intermediates in catalytic processes, but little is known about these species. The high-energy physics community is showing rapidly increasing interest in the ionization of liquids and needs to know the behavior of the ions and electrons involved. These areas can be studied by pulse radiolysis. Current studies include: (1) the reaction kinetics and equilibria of electrons in dielectric liquids under high pressures, which help explain the nature of electron capture and the role of electrostriction; (2) the hall mobility of electrons (mobility of electrons in the untrapped state) in dielectric liquids, where the extent of trapping in the liquids can only be estimated by knowing about the untrapped state; (3) the stability and reactions of Fe(IV) and Fe(V) complexes in aqueous solutions; (4) the kinetics and equilibria of interconversion of cobalt hydrides, CO₂, and CO complexes in aqueous solution; and (5) the application of a transient circular dichroism technique in pulse radiolysis studies of reactions involving structural changes of optically active intermediates. [7.9 FTE]

13. Photochemical Transformations in Bacteriorhodopsin
S. Seltzer

The aim of this research is to elucidate important factors in the mechanism used by the purple membrane for converting solar energy to chemical energy. When light is absorbed by bacteriorhodopsin, the protein pigment of the membrane, protons are pumped through the membrane, resulting in the formation of a proton gradient. The proton translocation process is completely dependent on reversible *cis-trans* isomerizations of retinal, the bound chromophore of the pigment. Photon absorption initiates a cycle wherein retinal is isomerized in the first step. Proton translocation and retinal reversion occur in subsequent nonphotolytic steps. The manner in which these *cis-trans* isomerizations are driven is currently being investigated. Theoretical calculations support the hypothesis that *cis-trans* isomerizations of bound retinal are catalyzed by a neighboring carboxylate anion of an aspartate residue of bacteriorhodopsin via an electrostatic or nucleophilic interaction mechanism. Compounds containing an amino group for Schiff base formation with retinal and a tethered carboxylate group have been synthesized to mimic the binding site of retinal in bacteriorhodopsin. These systems are being examined for activity in retinal isomerization. [1.4 FTE]

14. Thermal and Photoinduced Reactions of Metal Complexes

*N. Sutin, C. Creutz, B.S. Brunschwig,
J. Winkler, E. Fujita*

The design of molecular systems that will efficiently generate and maintain a photoinduced charge separation requires a thorough understanding of the factors that control electron-transfer rates. This project involves fundamental experimental and theoretical studies of these factors. The roles of distance, nuclear configuration, free-energy changes, and solvent dynamics (in inter- and intramolecular electron-transfer processes) are being elucidated through studies of transition-metal complexes. The efficient photogeneration of fuels also requires the coupling of one- and multielectron transfer processes and the stabilization of reactive intermediate fragments. This project also encompasses fundamental chemical and mechanistic studies of catalytically promising transition metal centers in high and low oxidation states. The thermal- and photoinduced oxidation of water and the reduction of water and CO₂ are being studied. [9.6 FTE]

15. Energy Transfer in Chemical Kinetics

R.E. Weston, J.M. Preses, G. Hall

Rates and pathways of energy transfer in atomic and molecular collisions are important components of many reaction mechanisms. This project is directed toward the experimental study of energy flow in collisions. Energetic atoms or molecules are prepared with excess translational, vibrational, or electronic energy by pulsed laser radiation. Time-resolved spectroscopy (diode laser absorption, laser induced fluorescence, or spontaneous infrared fluorescence) of the initially excited species or a collision partner measures the loss or gain of energy as a result of collisions. In current work, the vibrational populations of CO formed in the reaction of hot H atoms with CO₂ are being determined. Doppler techniques are being developed to investigate orientational effects in inelastic collisions. In addition, vacuum-ultraviolet radiation from the dynamic spectroscopy beamline of the National Synchrotron Light Source (NSLS) is used to study electronically excited states of molecules and photoionization of atoms. Recent experiments at the NSLS have determined mechanisms of electronic energy relaxation in cyclohexane isolated in rare gas matrices. Some assistance to outside users of the NSLS is also provided by this project. [6.9 FTE]

16. Hot Atom Chemistry

A.P. Wolf, R.A. Ferrieri

The project objective is to understand the chemical mechanisms involving translational and/or electronic energy transfer between highly excited atoms and substrate molecules. Accomplishments include the recent development of a novel sputtering atom source for generating hot oxygen atoms in well-defined states at controlled energy levels, and the implementation of classical nucleogenic methods for generating other hot atoms of interest. Recent interest in the reactions of hot oxygen atoms with unsaturated substrate molecules stems from the realization that high-temperature hydroxyl radical formation from such systems is one of the fundamental aspects of oxygen atom chemistry not clearly understood. We have shown that these species are formed at levels of increasing importance as the energy of the system increases. Other active areas of research include studies on the effect of translational energy on the deactivation mechanisms for electronically excited nitrogen atoms, the

stereochemical consequences of hot homolytic halogen atom substitution reactions, and the mechanisms of carbon atom reactions. [3.2 FTE]

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

Chemical Biodynamics Division

\$990,000

17. Artificial Photosynthesis

M. Calvin, J.W. Otvos

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 our 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 three areas. (1) The useful fraction of the total solar spectral irradiance must be increased. At present, with resonance absorbers like dyes and other chromophores, only narrow spectral regions are useful. It is obvious that a series of relatively narrow-band sensitizers could be arranged to take advantage of the full solar spectrum. (2) 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. Our search will continue for chemically stable materials that can serve as separation barriers and that are also permeable to electron transport. (3) 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. [3.5 FTE]

18. Chemistry with Near-Infrared Photons

H. Frei

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 lend a basis for new concepts for chemical storage of near-infrared photons, their conversion into electrical energy, and use in photocatalysis. Emphasis is on the elucidation of elementary reaction steps, since the insight gained allows the identification of relevant chemical systems. Therefore, time-resolved emission and absorption spectroscopy are used for the study of redox chemistry in aqueous solution. The most recent example is the elucidation of the mechanism of oxidation iodide to iodine by singlet delta O₂, a reaction that may allow conversion of the electronic energy of the excited O₂ into electrical energy. Other reactions are initiated in an inert gas matrix in

order to elucidate reaction paths by trapping chemical intermediates. FT-infrared spectroscopy is used to determine structures of intermediates and final reaction products. With this technique, observations have been made of the first chemistry of singlet SO, and stereoselective photooxidation of alkenes to epoxides by nitrogen dioxide. [1.2 FTE]

19. *Chemistry of Electronically Excited Molecules* G.C. Pimentel

Both natural and artificial photosynthetic processes depend on the special chemistry of electronically excited molecules. Consequently, a full understanding of chemistry and energy movement on electronically hypersurfaces is key to the development of better processes for the storage of photon energy in the form of chemical bonds. Cryogenic solids permit study of light initiated study and differentiation between primary photolysis products, normally transient intermediates and secondary photolysis products. Progress has been made in controlling reaction branching with the matrix environment via controlled singlet-triplet surface crossing through external atom spin-orbit coupling. Fluorescence and phosphorescence spectra and lifetimes again reveal singlet-triplet crossing. Nanosecond infrared spectroscopy permits direct detection and kinetic study of electronically excited molecules. Chemical systems under matrix study include mercury, cadmium, and zinc atom photoreactions with haloalkenes and haloalkanes, photochromic molecules, tuned laser mapping of electronic hypersurfaces, fluorescence and phosphorescence of dimethylaminobenzonitrile, and spectra and kinetics of gaseous free radicals and excited-state molecules. [6.0 FTE]

Materials and Chemical Sciences Division \$400,000

20. *Photochemistry of Materials in the Stratosphere* H.S. Johnston

This research is concerned with fundamental gas-phase photochemistry and with global atmospheric photochemical modeling. One goal is to measure the distribution of excess energy in the fragments produced after a molecule is broken apart by an energetic pulse of light. Another goal is to obtain optical and kinetic data in the laboratory that are needed by modelers of the atmosphere. The experimental methods include laser flash photolysis, laser resonance absorption, resonance fluorescence, dispersed chemiluminescence from photolysis products, and infrared diode lasers. Quantum mechanical studies are made of the molecular structure of certain atmospheric molecules, and other theoretical model studies are made of global atmospheric photochemistry. This research has applications to molecular dynamics, to problems of atmospheric ozone, and to problems of global change of trace gases in the atmosphere. [5.0 FTE]

21. *Photon-Assisted Surface Reactions, Materials, and Mechanisms* G.A. Somorjai

This project explores the surface science of photocatalyzed chemical reactions that take place at the solid-vapor and solid-liquid interfaces. Focus is on processes that thermodynamically could not occur without the presence of light as the energy source. The photodissociation of water to produce hydrogen and oxygen, of nitrogen to form ammonia, and of carbon dioxide to produce formic acid is investigated. The catalysts are semiconductor surfaces that absorb and convert light

to separated, excited electron-electron vacancy pairs that initiate the reduction and oxidation of adsorbed species. The materials that are being used include iron oxides, silicates, and silicon carbide. The purpose of these studies is to explore the elementary steps of the photon-assisted surface reaction by a combination of modern surface science techniques and then to establish the optimum conditions (of surface structure, composition, temperature, and reactant mixture) to maximize the rate of production of desired chemicals. [2.3 FTE]

Notre Dame Radiation Laboratory University of Notre Dame Notre Dame, Indiana 46556

\$3,100,000

22. *Quantum Mechanical Studies of Radiation-Produced Intermediates*

D.M. Chipman, I.C. Carmichael, J. Bentley

Electronic structure calculations are being used to theoretically characterize the microscopic properties of matter, emphasizing applications to transient species such as free radicals and electronically excited molecules. These dominate the early processes initiated by radiolysis and photolysis of various media and also occur as important intermediates in many chemical reactions. As an aid to the interpretation of relevant experimental studies, molecular structures and properties such as vibrational frequencies, hyperfine coupling constants, and lifetimes are being determined by *ab initio* method. Recent work includes a benchmark calculation of the isotropic hfc constants of the first-row atoms with open-shell p electrons, establishing the correlation and basis set requirements for quantitative prediction of hfc constants in these systems. Extension of these findings to molecular pi radicals is being undertaken. Hyperfine interaction tensors have been calculated for the difluorine radical anion, resolving a striking disagreement between experiment and existing theory. Vibrational effects on magnetic coupling constants in radicals derived from first- and second-row trihydrides have been estimated, and the reported anisotropic splitting in the silyl radical has been called into question. Using He²⁺ (3s3p) as a prototype system, a new method to calculate lifetimes and energies of electronically excited metastable systems by analytic continuation of real-valued electronic energies is being extended to the situation where multiple decay channels are possible. [1.8 FTE]

23. *Inorganic Photochemical Processes* G.J. Ferraudi

The dynamics of excited- and ground-state redox reactions in coordination complexes is being investigated under magnetic fields between 0 and 9 Tesla. In these conditions, the magnetic field is dually regarded as a Zeeman perturbation of the orbitally degenerated electronic levels in reactants and products or as a dynamic perturbation along the reaction coordinate. In either case, such perturbations are used as probes of the electronic matrix element coupling initial and final states of various kinds of reactions (e.g., radiationless relaxations of excited states, inner and outer sphere electron transfers, and characteristic excited-state reactions). Some of the compounds considered in these studies (e.g., metal clusters and macrocyclic complexes) require further characterization of their excited-

state properties. Such work is conducted using pulsed techniques (i.e., flash photolysis and pulse radiolysis), while sequential biphotonic excitations are being used for the photochemical characterization of "phantom" states. These photochemical and photophysical studies are conducted with compounds that exhibit direct or sensitized redox reactivity for excitations in the visible region of the solar spectrum and, hence, exhibit potential applications in solar photochemistry. [6.3 FTE]

24. *Microwave Studies of Radiation-Produced Radicals*

R.W. Fessenden, K.P. Madden

Electron spin resonance (ESR) is used to study the structures, interactions, and reaction dynamics of free radicals formed by *in situ* radiolysis and photolysis. The spectra obtained provide definitive radical structures and such details as acid-base properties. Reaction mechanisms can be deduced from the identity of the radicals and their chemical transformations. Time-resolved experiments with pulsed radiation allow measurement of radical reaction rates as well as rates of spin polarization and relaxation that define the range of electron spin interactions involved in chemical bonding. Measurements on rates of spin trapping are being extended to a variety of radicals and traps to provide data of value to those who use this technique in various chemical systems. Time-resolved studies of microwave dielectric absorption determine the degree of charge separation in photochemical intermediates in order to explain changes in reaction mechanism with solvent polarity. Experiments are in progress to determine how the dipole moments of excited complexes (exciplexes) vary with solvent characteristics. Microwave absorption is also used to measure the yield, properties, and kinetics of charge carriers photoinjected into semiconductor particles and films from sensitizers. [11.5 FTE]

25. *Photochemical Processes Following Core Electron Excitation*

R.G. Hayes

Selective excitation of molecules by excitation of a core electron, using photons in the 100 to 500 eV energy range from the National Synchrotron Light Source, is used to prepare highly excited states with a localized excitation. The photochemical processes of these states, in particular the production of ionic fragments, are observed. Complete data have been obtained on photofragmentation of CS₂ upon excitation about the S 2p edge, including electron-ion coincidence data, which give the abundances and kinetic energies of various ions in coincidence with Auger electrons having particular kinetic energy. It is striking that the kinetic energy that is released in the fragmentation to CS⁺ plus S⁺ (which is the most important fragmentation process) is independent of the state of the molecular ion. The independence extends to states that have as much as 12 eV of excitation above the ground state of the molecular dication. Ion-ion coincidence data have been obtained by excitation of methanol about the C 1s edge to complement previous data on this system. These data confirm that the first step in the decay of the methanol dication is proton loss. [0.3 FTE]

26. *Photochemical and Photoelectrochemical Processes for Light-Energy Conversion*

P.V. Kamat

Fundamental aspects of light-energy conversion and storage are being investigated in photochemical and photoelectrochemical

systems. Photoelectrochemical processes such as photosensitization, phototransformations of adsorbed species, and photocorrosion at single crystal and colloidal semiconductor are investigated. The aim of this work is to elucidate the mechanistic features and kinetic details of interfacial charge transfer processes. Optical effects caused by trapped charge carriers in semiconductor colloids, such as metal sulfides and selenides, are characterized with laser flash photolysis and pulse radiolysis. Investigation of these trapped charged carriers is important because they can greatly influence the photocatalytic activity and surface corrosion of the semiconductor. Photosensitized charge injection processes in opaque semiconductor powders and photoinduced charge separation on opaque metal oxide particles are being investigated by diffuse reflectance laser flash photolysis. Such *in situ* measurements are important in obtaining mechanistic and kinetic details of photoelectrochemical reactions involving nontransparent semiconductor systems. Spectroelectrochemical experiments are also performed to investigate the role of photoactive compounds in modifying the properties of semiconductor electrodes. [4.7 FTE]

27. *Statistical Theories of Reacting Systems*

J.J. Kozak

A comprehensive theory of reactions in nonhomogeneous media is under development. Particular emphasis is directed toward determining the dynamics and efficiency of photoinduced water cleavage reactions. The literature provides extensive experimental studies of photoinduced reactions between a sensitizer, S, and electron acceptor, A, of the type, $S + A \rightarrow S^+ + A^-$, followed by water cleavage, as mediated by a colloidal catalyst and/or nonhomogeneous environment (a zeolite, clay vesicle, micelle, or monolayer). Such studies provide an extensive bank of data against which predictions of theory can be tested. Therefore, solution of the underlying stochastic master equation for such systems and comparison with existing experimental data allow one to assess the importance of such factors as system dimensionality and geometry, compartmentalization and coverage of the catalyst, pH and the influence of counterions, and the role of intermediates. Once these physical and chemical factors are clearly understood and their influence quantified, a principal goal of the work is to use this information to design and then examine, via computer simulation, the consequences of new reaction system geometries and/or experimental conditions that can lead to an enhancement in the production of hydrogen. [1.3 FTE]

28. *Track Effects in Radiation Chemistry*

J.A. LaVerne, A. Mozumder, N.J.B. Green, R.H. Schuler

The chemical effects of the track structure produced by ionizing radiation in various liquid media are being studied using experimental and theoretical methods. Experiments are focused on radiation chemical studies with heavy ions. Radiolytic yields are determined as a function of particle type, energy, linear energy transfer (LET), and local energy deposition. Using the facilities of the Notre Dame Nuclear Structure Laboratory, these studies are being conducted with a variety of heavy ions having LETs of 10 to 1000 eV/nm. Studies with ions of up to 5000 eV/nm are conducted at the Argonne National Laboratory ATLAS facility. With experimentally available inelastic cross sections, track models are being developed to determine the distribution

of energy deposited in spurs generated by electrons and heavy ions. The initial yields and distributions of ions and excited species are then estimated and the subsequent temporal variation is interpreted by means of stochastic diffusion-kinetic models for isolated spurs and deterministic models for heavy particle track cores. Models for determining ionization yields produced by ionizing radiation in liquid argon and anthracene are being developed. [4.7 FTE]

29. Influence of Ordered Molecular Assemblies on Photochemical Processes
L.K. Patterson

The effects of molecular organization on processes involving photochemical and radiation chemical induced intermediates are investigated in ordered heterogeneous systems such as micelles, vesicles, and monolayers. These studies are directed toward determining the extent to which such systems may be used to exercise kinetic control over reactions of interest, especially in solar energy storage. At present, the work is focused on spread monolayers at the air-water interface because these provide the best means for simultaneously controlling and monitoring the thermodynamic state of the system. Time-resolved and steady-state fluorescence techniques are used to measure lateral diffusion, rotational mobility, energy transfer, and permeability in various lipid structures under changing conditions of organization. Reflectance is being used to monitor spectra of nonfluorescent species such as porphyrin aggregates. Flash photolysis and product analysis by HPLC are used to determine kinetics of photoperoxidation in micelles and monolayers, and to determine the influence that molecular organization can have on mechanisms involved. Such studies should provide information on the pathways by which lipid structures used for compartmentalization of reactions may undergo photoinduced degradation. [7.0 FTE]

30. Radiation Chemistry Data Center
*A.B. Ross, W.P. Helman, G.L. Hug,
I.C. Carmichael*

The Radiation Chemistry Data Center (RCDC) compiles and evaluates data on photochemical, photophysical, and radiation chemical processes. Kinetic, spectroscopic, and thermodynamic data for primary processes involving excited states and radicals in solution are compiled and evaluated in collaboration with scientists from other laboratories. Data bases are assembled and used to prepare a variety of publications, such as data tables and bibliographies, and to provide reference services. A chemical registry file (RCDCreg) is maintained for chemical species represented in the numeric data files. The RCDC Bibliographic Data Base (RCDCbib), maintained since 1966, is used to produce the current-awareness publication, *The Biweekly List of Papers on Radiation Chemistry and Photochemistry*. On-line access is available to RCDCbib and to numeric data bases covering (1) rate constants for about 6,000 reactions involving inorganic radicals in aqueous solution and (2) triplet-triplet absorption spectral data for over 1,100 organic molecules in condensed phases. Other data which have been collected include reduction potentials for about 700 couples involving radicals in aqueous solution, photophysical data for about 1,800 organic molecules, and quenching rates for excited states of metal complexes with about 1,000 organic and inorganic quenchers in solution. [3.0 FTE]

31. Radiation-Induced Chemical Reactions

R.H. Schuler, G.N.R. Tripathi, L.K. Patterson

A wide variety of radiation chemical systems are being examined using Notre Dame Radiation Laboratory's broad base of highly developed instrumental methods. Pulse radiolysis with detection by absorption, conductivity, ESR, and laser Raman techniques is used to characterize transient behavior, while steady-state irradiation and analysis by such methods as HPLC are being used to determine ultimate products of reaction. Currently, considerable emphasis is being given to time-resolved resonance Raman measurements on prototype radiation-generated oxygen- and nitrogen-containing radicals in aqueous solution. Focus is on the proton and electron exchange properties of these radicals. Laser flash photolysis studies of radicals produced by pulse radiolysis are being conducted to examine photochemical properties of radical excited states. Studies of second-order radical reactions are being conducted at very high pulse intensities, using a Febetron as the radiation source and chromatographic methods to determine the products. Inter-ring electron transfer in polycyclic aromatic systems is being investigated using pulse radiolysis and chromatographic methods. [12.7 FTE]

32. Organic Photochemical Processes

D. Weir, G.L. Hug

The physical and chemical properties of reaction intermediates produced in condensed phases upon photoexcitation of organic compounds are being investigated. Experimental methodologies used to probe these intermediates include picosecond and nanosecond laser flash photolysis, pulse radiolysis, and diffuse reflectance. These studies produce spectral identification and absolute reaction rates of the short-lived organic reaction intermediates for such common organic photoreactions as radical hydrogen abstraction, photodimerization, photoenolization, di- π -methane rearrangement, ring expansion, electron transfer, and energy transfer. Model compounds include alkyl and aryl carbonyls, substituted ethylenes, arylmethyl halides, dienes, aromatic heterocycles, and polycyclic aromatic compounds. Of specific current interest are the reactions of arylmethyl radicals in photoexcited states and the effects of unusual spin multiplicities on energy and electron-transfer reactions. Also of interest are studies of organic reactions on solid surfaces. Diffuse reflectance measurements provide observation of reaction intermediates on or in solid opaque materials. Using this technique, studies of molecular mobilities on surfaces and modification of organic photoreactions on inorganic oxides (SiO_2 , Al_2O_3 , TiO_2) are conducted. These studies provide basic understanding of organic reactions and may be useful in developing methodologies for the control of reaction rates, product yields, and product distributions. [6.3 FTE]

Solar Energy Research Institute
Golden, Colorado 80401

Solar Fuels Research Division

\$900,000

33. Model Systems for Artificial Photosynthesis

J.S. Connolly

This project focuses on fundamental aspects of light-induced electron transfer in donor-acceptor systems designed to mimic the primary photoprocesses in reaction centers of photosynthetic

organisms. To date, the work has concentrated on studies of covalently linked porphyrin-quinone molecules and their unlinked constituents in order to sort out the effects of some of the factors that influence both forward and reverse electron transfer. These factors include the photophysical and spectroscopic properties of the donor, the redox potentials of the donor and acceptor, the distance and orientation imposed by the linking bridge, the nature of the surrounding medium, and the temperature. The emphasis of this research has been expanded recently to include studies of how the medium (solvent or solid-state matrix) influences the rates and mechanisms of excited-state quenching processes, specifically how the local dielectric environment affects the energetics for electron transfer. The molecular environments of interest include organic solvents of varying dielectric strength and polymer matrices, both synthetic and biological. The goal is to understand the specific properties of protein membranes that facilitate electron transfer and stabilize the resulting redox products in natural photosynthesis. [2.3 FTE]

34. Modified Semiconductor Electrodes for Solar Energy Utilization
A.J. Frank

Basic research is being conducted on the chemistry and physics of *conductive polymers and the solid-state and electrochemical properties of the semiconductor-conductive polymer junction*. X-ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy of poly(3-methylthiophene) (PMeT) have provided insight into the electronic and physical changes that accompany PF_6^- doping. The PF_6^- anion is found (1) to cause structural disorder along the carbon backbone and (2) to interact with the lone-pair electrons of sulfur. The electronic structural changes induced by doping indicate formation of bipolaron bands, as theoretically predicted. The photoemission spectra show changes in work function upon doping and behavior that is not typical of a classical metal. Schottky barrier formation between n-CdS and PMeT has been demonstrated. The rectification ratio, barrier height, quality factor, and other junction characteristics of PMeT:n-CdS are comparable to metal:n-CdS solid-state Schottky barrier cells. Dramatic changes in the junction characteristics are observed and accounted for when the PMeT:n-CdS solid-state device contacts an aqueous electrolyte. The first observations were made of Fermi-level movement in a conductive polymer coating and Fermi-level pinning in PMeT:n-CdS liquid junction cells. A better understanding of interfacial charge transfer and photocorrosion in conductive polymer modified electrodes has been achieved. [1.5 FTE]

35. Basic Photoelectrochemistry Research
A.J. Nozik, J.A. Turner

Research in photoelectrochemistry is being conducted on size quantization effects in superlattice photoelectrodes and in very small semiconductor colloidal particles. A new metallorganic chemical vapor deposition (MOCVD) has been installed to prepare superlattices and various quantum well structures for photoelectrochemical applications. Photomodulated reflectance and transmittance spectroscopy have been introduced into this laboratory, and found to provide excellent critical information on quantized energy level spacing and structure quality. A theoretical model for the behavior of superlattice photoelectrodes has been developed further, including important effects caused

by miniband formation and electron delocalization. For the first time, quantized colloids of the layered dichalcogenides MoS_2 , WS_2 , and WSe_2 have been formed. Detailed studies of the layered HgI_2 system have proven that colloidal particles with tetrahedral bonding are formed, and not just ionic or molecular complexes. A new and simple method for producing quantized particles in silicate glasses has been developed; the spectra of a variety of colloidal particles in liquids and glasses are identical. [4.3 FTE]

Chemical Physics

Ames Laboratory
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\$675,000

36. Statistical Mechanics of Nonequilibrium Systems
D.K. Hoffman

New classical, semiclassical, and quantum mechanical scattering theories for reactive collisions between gas-phase molecules are devised and incorporated into a statistical mechanical development of the kinetic theory of reactive polyatomic gases. This work provides powerful methods for investigating reaction dynamics in systems of importance in combustion. Another activity involves developing new, efficient methods for accurately predicting interaction energies in small and large molecular clusters. Finally, the dynamics and statistics of distributions of molecules adsorbed on surfaces under nonequilibrium conditions are analyzed via master equations and computer simulation. Such a theory is important for the appropriate interpretation of surface spectroscopic data. This analysis incorporates the effect of interactions between adsorbed surface species on the selection of binding sites, a study of island formation via direct adsorption and surface migration mechanisms, and adsorbate effects on the catalytic properties of surfaces. [2.0 FTE]

37. Molecular Beam Photoionization and Photodissociation Studies of Molecules, Clusters, and Radicals
C.Y. Ng

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. 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. [5.75 FTE]

38. *Molecular Bonding Theory* K. Ruedenberg

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. 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 (e.g., minima, saddles, valleys, bifurcations) cannot be simply rationalized, rigorous explanations in terms of electronic rearrangements are needed. Consistent general methods are developed for an in-depth analysis of *ab initio* electronic wave functions, leading to the recognition of atoms in molecules, to the identification of interatomic interactions, and to the relations between energetic interactions and electronic rearrangements. Oxidation-reduction reactions, exchange reactions, and isomerizations relevant to combustion, hydrogenation, or atmospheric problems are investigated. [3.0 FTE]

Argonne National Laboratory Argonne, Illinois 60439

Chemistry Division

\$4,028,000

39. *Photoionization-Photoelectron Research* J. Berkowitz

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. The free-radical studies are providing accurate information on important thermochemical quantities, such as heats of formation of SiH_n , NH_n , PH_n , AsH_n , and SeH_n species, their corresponding bond energies, and the bond energies for $\text{H}_3\text{C}_2\text{-H}$ and $\text{H}_3\text{B-BH}_3$. Unusual geometrical structures such as bridged B_2H_5^+ ; classical and nonclassical structures of C_2H_3^+ ; and SiH_4^+ far from tetrahedral are inferred from these studies. Conventional He I and threshold photoelectron spectroscopy are used to measure the spectroscopic properties of 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 clearly distinguish between isomeric molecular ions. [3.8 FTE]

40. *Chemical Dynamics in the Gas Phase* T. Dunning, Jr., R. Bair, M. Davis, L. Harding, R. Shepard, A. Wagner, K. Liu, R. MacDonald, J. Michael, J. Hessler

The project objective is to characterize the energetics, dynamics, and mechanisms of elementary chemical reactions in a comprehensive manner, emphasizing reactions of importance in the oxidation of simple fuels. The project combines an ongoing theoretical effort with a new experimental initiative in chemical dynamics and kinetics. The theoretical effort focuses on calculating accurate reaction energetics and potential energy surfaces, determining the dynamics of reactions on the computed surfaces, and developing the mathematical/computational methodology needed to accurately model molecular systems. The experimental initiative emphasizes (1) shock tube studies of the kinetics of reactions over the temperature range from 800 K to 2500 K, using both flash photolysis-resonance absorption and state-of-the-art laser techniques; and (2) molecular beam studies of the dynamics of reactions using crossed, pulsed beam, and laser spectroscopic techniques capable of both angle- and state-resolved measurements. [15.5 FTE]

41. *Metal Cluster Chemistry Research* S.J. Riley, E.K. Parks, J. Jellinek

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, nickel, niobium, aluminum, chromium, vanadium, rhodium, titanium, 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 and changes in structure with cluster size. 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 photophysical processes are probed. These experimentally determined cluster properties are correlated with theoretical calculations. Ultimately, these studies will provide a better understanding of surface chemistry and heterogeneous catalysis. [7.6 FTE]

Brookhaven National Laboratory Upton, Long Island, New York 11973

Department of Applied Science

\$560,000

42. *Combustion Kinetics and Reaction Mechanisms* R.B. Klemm, J.W. Sutherland

This multitechnique research project focuses on the investigation of combustion kinetics and mechanisms of elementary reactions. The project addresses two main objectives: (1) the measurement of absolute rate constants for atom/molecule and radical/molecule reactions over a wide temperature range; and (2) the mechanistic study of gas-phase combustion and pollutant formation processes. Emphasis is on reactions involving a wide range of fuels (including hydrogen, alcohols, and hydro-

carbons) and combustion intermediates (e.g., aldehydes and olefins). At present, the project features the following experimental techniques: (1) flash photolysis-resonance fluorescence (FP-RF), 200 to 1100 K; (2) discharge flow-resonance fluorescence (DF-RF), 300 to 1200 K; (3) flash photolysis-shock tube (FP-ST), 800 to 2500 K; and (4) discharge flow-mass spectrometry (DF-MS). The first three methods are used in a complementary way to determine specific rate constants for elementary reactions. This multitechnique approach provides a unique capability for performing kinetic measurements over the exceptionally wide temperature span, 200 to 2500 K, with high reliability. The DF-MS experiment was constructed recently to perform branching ratio measurements for multichannel elementary reactions. This device is designed to identify primary reaction products sampled via a molecular beam from a flow tube. Additionally, this DF-MS experiment has the capability of using vacuum ultraviolet radiation at the National Synchrotron Light Source to perform photoionization MS and thus achieve enhanced sensitivity and selectivity. [5.6 FTE]

Chemistry Department **\$3,080,000**

43. Theoretical Chemistry
S. Ehrenson, J.T. Muckerman, M.D. Newton

This work explores structure and dynamics pertinent to energy storage, solvation, and charge transfer in complex chemical systems, and the energetics and dynamics of molecular collision phenomena. One objective of this research is to formulate and implement techniques for elucidating structural, thermodynamic, and dynamical properties of complex chemical systems, relying heavily on large-scale *ab initio* electronic structure techniques and dielectric response theory. Emphasis is on mechanistic analysis of the trapping or transport of excess charge in condensed phases (especially electron transfer processes associated with transition metal complexes in polar fluids). Both the geometrical and electronic structural aspects of the theoretical research are strongly coupled to a variety of experimental probes, including those represented by the major structural facilities at BNL. The theoretical studies help to interpret these experimental data, to facilitate their use in mechanistic kinetic analyses, and to suggest useful areas for new experiments. Another objective is to develop theoretical approaches and computational methods for elucidating state-to-state collision phenomena (with major emphasis on gas-phase reactive collisions involving a small number of atoms), and to apply these methods to systems of experimental interest in a variety of disciplines. An important facet of this work involves the characterization of potential energy surfaces governing various chemical reactions. A new aspect of this research in molecular dynamics focuses on properties of molecules adsorbed on solid surfaces. [5.1 FTE]

44. Energy Transfer Studies in Cluster Impacts
L. Friedman, R.J. Beuhler

This research project is concerned with energy transfer and related chemical processes in very high energy density assemblies generated by impacts of clusters on solid surfaces. Energy densities corresponding to temperatures as high as one million degrees K can be generated in assemblies of thousands of atoms by the impact and penetration of 300 keV clusters containing between 50 and 250 atoms. These atomic assemblies cool either by thermal conduction or by the ejection of hot atomic or molec-

ular particles. A study of the gaseous products of cluster impact provides information on the relative importance and the mechanisms of the cooling processes. The initially formed collision spike, in cooling by conduction, creates a larger assembly of very energetic atoms that can participate in chemical reactions with very high kinetic barriers. Techniques have been developed for the determination of mass distributions and kinetic energies of gaseous products of cluster impacts. The sputtering of molecular ion fragments has been observed from carbon, copper, and gold targets, which indicates a correlation between fragment size and binding energy in these systems. Kinetic energy determinations on sputtered products should provide information on projectile stopping power and the magnitude of initial energy densities. [4.5 FTE]

45. Gas-Phase Photoionization and Photoelectron Spectroscopy of Molecules and Clusters
J.R. Grover, M. White, L. DiMauro

The general aim of this project is the experimental characterization of the dynamics of optically prepared excited and ionic states of molecules, radicals, and clusters. Intense synchrotron and laser radiation sources are used to induce such processes as dissociation, dissociative rearrangement, and autoionization, the products of which are probed by a variety of photoionization-based techniques. Current research activity is centered on: (1) application of circular dichroism in photoelectron angular distributions as a probe of molecular spatial orientation with particular emphasis on photofragment alignment and collisional depolarization; (2) systematic investigations of superexcited Rydberg states of molecules by vibrationally resolved photoelectron and photoion fluorescence techniques; (3) studies of endothermic photoionization-induced dissociative rearrangement and self-reaction processes in van der Waals heterodimers and heterotrimers; (4) systematic study of the behavior of isolated atoms and molecules in an intense laser field, using angularly resolved electron spectroscopy to examine the nonresonant multiphoton ionization of alkaline earth atoms in the intensity regime of 10^{13} to 10^{10} W/cm²; and (5) development and construction of a laser-synchrotron radiation facility at the NSLS which will couple the unique capabilities of dispersed synchrotron radiation (tunability, energy) and lasers (bandwidth, intensity) for the study of time- and state-resolved photochemical dynamics. [6.3 FTE]

46. Chemical Crystallography
T.F. Koetzle, A. Kvick, R.K. McMullan

In the chemical crystallography project, the complementary techniques of neutron and x-ray diffraction are used to provide essential structural data for a wide variety of substances of importance to energy systems. The combined power of the National Synchrotron Light Source (NSLS) x-ray crystallography station and the High Flux Beam Reactor (HFBR) neutron diffraction facilities is being exploited to open up new areas of research. The ultimate objective is to provide theoretical and synthetic chemists with structural data required to understand the unique properties of substances used in energy conversion systems and to guide in the synthesis of new substances with specific functionality. Recent results include the first structure determination based on three-dimensional x-ray data collected at the NSLS station, for a single 30 μ m microcrystal of the catalytically interesting high-silica sodalite with an organic template (ethylene glycol) in the center of the

sodalite cage. At the HFBR, accurate neutron diffraction studies of two Fe(II) dihydrogen complexes, which define the geometry of the intact η^2 -coordinated H_2 ligands, were completed within the past year. These complexes serve as models for intermediates in the oxidative addition of H_2 to a metal center, and are of considerable importance in understanding the activation of dihydrogen by metal-based catalyst systems. [5.8 FTE]

47. Spectroscopy and Structure of Short-Lived Intermediates
T. Sears

High-resolution molecular spectroscopy is used to measure the structure and reactivity of molecular fragments in gas phase chemical reactions. The data provide information on species whose reactions often govern the course and rate of gas phase processes. In addition, the spectroscopic data are necessary precursors to future precise measurements of chemical reactions on a state-by-state basis. Most recently, ultraviolet laser flash photolysis has been used as a clean source of small free radicals, in particular small hydrocarbon fragments such as methyl (CH_3), ethyl (C_2H_5), and methoxy (CH_3O). The radicals formed in the photolysis reaction are detected by means of their infrared absorption spectrum, using a low-power tunable infrared laser source. This technique allows the measurement of the vibration-rotation spectrum of the radical with extremely high precision. The data obtained are used to estimate the detailed molecular structure, often including electron spin fine structure effects, and the intramolecular potential surface. The distribution of the available photoproduct energy among the energy levels of the radical also provides information on the nature of the surface on which the photoreaction is occurring. [4.0 FTE]

Lawrence Berkeley Laboratory
University of California
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Applied Science Division **\$155,000**

48. Combustion Chemistry
N.J. Brown

Combustion processes are governed by chemical kinetics, energy transfer, transport, and fluid mechanics, and the complex interactions among these. Understanding chemical kinetics and energy transfer offers the possibility of better understanding combustion so that it can be controlled. In all chemical changes, the pathways for energy movement are determining factors. Competition among these pathways, including energy dissipation, determine product yields, product state distributions, and the rate at which reaction proceeds. In this project the dependence of reactivity and energy-transfer processes on various types of energy, angular momentum, and potential energy characteristics is investigated. Dynamical and statistical theoretical approaches are being pursued using realistic potential energy surfaces for prototypical molecular systems important in combustion systems. Recent research has been concerned with the application of functional sensitivity analysis to determine the relationship between dynamic observables and the potential energy surface. This has revealed important information about energy-transfer processes. [1.0 FTE]

Materials and Chemical Sciences Division **\$2,250,000**

49. Energy Transfer and Structural Studies of Molecules on Surfaces
C.B. Harris

The goals of this research are (1) to study the mechanisms responsible for transfer of energy from the excited states of molecules to metal surfaces and (2) to develop new laser techniques for probing molecule-surface interactions. The research is both theoretical and experimental, and includes nonlinear optical and picosecond laser techniques in addition to a variety of standard surface science tools for characterizing molecule-surface interactions. Recent work has centered on the development of picosecond infrared lasers, the elucidation of the mechanism of surface-enhanced photochemistry, surface-enhanced photoelectron emission, and the breakdown of classical dielectric response theory for explaining energy transfer from molecules to noble metal surfaces. The latter studies have resulted in a classification scheme in which molecular excited states that produce intraband electronic excitations transfer energy to electrons localized near the metal surface, while those excited states that can access direct interband excitations transfer energy to electrons throughout the bulk of the metal. Results have a direct bearing on high-speed technological devices and materials and on other problems of general interest (e.g., the dynamics of electrical transmission in conductors on ultrafast timescales and the optical properties of thin films). [1.5 FTE]

50. Molecular Structure and Chemical Dynamics
Y.T. Lee, W.A. Lester, W.H. Miller, C.B. Moore, R.J. Saykally

The goal of the molecular structure and chemical dynamics program is to develop basic knowledge and understanding of chemical reactions, reactive molecules, and energy transfer. Such knowledge can provide a complete description of the processes of primary importance in combustion, atmospheric chemistry, and energy storage. The fundamental data obtained provide the basis for reliable chemical modeling of these complex systems. Spectra of transient species are recorded using lasers ranging from the far infrared to the vacuum ultraviolet in molecular beams and in gases. Structural, dynamical, and thermodynamic data are obtained. *Ab initio* calculations are conducted to guide searches for new spectra and to establish the conditions for which theory gives sufficiently accurate structural and energetic data. The rates of reaction and distributions of products are measured, often as a function of quantum state and relative velocity, for bimolecular reactions. Unimolecular reactions and rearrangements, tunneling dynamics, and photo-fragment energy state distributions are studied for molecules with fixed energy content. For termolecular reactions, the formation and stabilization of radical-radical reaction complexes are observed. Dynamical theories are developed and tested for these processes. Energy flow within a molecule is studied by laser spectroscopy. The goal is to understand energy transfer pathways and their interplay with chemical reaction pathways. These experiments, combined with dynamical theories, probe the possibilities for selective photochemistry. [28.8 FTE]

51. *Physical Chemistry with Emphasis on Thermodynamic Properties*
K.S. Pitzer

The project objective 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. Current emphasis is on novel ionic systems, and on properties close to the critical point. Systems comprising fused salts mixed in any proportion with water or other polar solvents are being studied experimentally and theoretically. Current studies also include (1) dilute ionic solutions very close to the critical point of the solvent where anomalous properties are observed and (2) the representation of near-critical properties in an equation of state valid over the full range of temperature and density. Recent theoretical advances include treatments of the dielectric constant of H₂O, the thermodynamics of ionic solutions in H₂O above its critical temperature, and the critical properties of pure ionic fluids such as NaCl. Earlier advances yielded improved equations for electrolyte solutions, which are now being applied to a wide variety of systems of industrial or geological interest (including geothermal brines). Recent efforts also include relativistic quantum chemistry of molecules containing very heavy atoms. [2.2 FTE]

52. *Photoelectron Spectroscopy*
D.A. Shirley

This project addresses both experimental and theoretical aspects of electron spectroscopy to investigate the electronic structure of matter in the gaseous and condensed phases. Research uses both laboratory sources at Lawrence Berkeley Laboratory and synchrotron radiation in the 5 to 5000 eV energy range available at the Stanford Synchrotron Radiation Laboratory, where there is participation in developing the spectroscopy of this newly accessible range of the electromagnetic spectrum. Time-of-flight measurements with synchrotron radiation are used to measure angular distributions of photoelectrons and resonant photoemission phenomena in the gas phase. Ultrahigh-resolution photoelectron spectroscopy based on molecular beams is yielding new information about small molecules and about the transition from single metal atoms to behavior characteristic of a three-dimensional solid. This project examines the electron structure of solids by using angle-resolved, variable-energy photoemission, and electron-energy-loss spectroscopy. The project also studies the geometric and electronic structure of surface-adsorbate systems using photoelectron diffraction, angle-resolved photoemission extended fine structure (ARPEFS), and surface extended x-ray absorption fine structure (SEXAFS). [10.0 FTE]

Lawrence Livermore National Laboratory
Livermore, California 94550

Division of Chemical Engineering **\$40,000**

53. *Chemical Kinetics Modeling*
C.K. Westbrook

The project objective is computer modeling of the chemical kinetics of combustion in laboratory and practical systems. Experimental data provided by a number of collaborating laboratories are analyzed using the numerical models and detailed

reaction mechanisms developed by this effort. Emphasis is on hydrocarbon fuels that are widely used in present combustion devices, such as furnaces and internal combustion engines. Construction and validation of comprehensive reaction mechanisms for these fuels will identify those elementary reactions on which the computed results are most dependent and that therefore merit the closest attention from experimental and theoretical research. Fuels being examined include iso-octane, n-heptane, acetone, ethanol, and the isomers of hexane and pentane. A particular goal of the current work is to assess the role that fuel molecular structure plays in determining overall rates of oxidation in engines, in cool flames, and in multistage ignition. [0.3 FTE]

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Chemistry Division **\$370,000**

54. *Molecular Research with Electron Spectroscopy*
T.A. Carlson, M.O. Krause

Photoelectron dynamics of free molecules and atoms is studied over a wide photon energy range by use of synchrotron radiation coupled with angle-resolved Auger and photoelectron spectroscopy. In several instances, the data for molecules are now sufficient to allow systematic comparisons among homologous series. Atoms include a variety of metal vapors, both open- and closed-shell, with emphasis on the behavior of d and f subshells. Multiplet effects in the outermost shell of open-shell atoms are examined in detail. Both molecular and atomic studies have revealed a number of phenomena requiring special attention: autoionization, the Cooper minimum, core-shell threshold effects, multichannel interactions, multiple excitation processes, shape resonances, and preionization resonances. Close interaction with coordinated theoretical calculations has given fundamental insights into the dynamics of the photoionization process, a basis on which to test molecular orbital theory, and a number of critical tests of many-body theory. Besides providing fundamental information in atomic and molecular sciences, the work supplies data and ideas for studying molecules adsorbed on surfaces, clarification of solid-state properties of metals, and an understanding of clusters. [2.1 FTE]

Sandia National Laboratories
Livermore, California 94550

Combustion Research Facility **\$2,075,000**

55. *Flame Dynamics Research*
R. Cattolica, W. Flower, R.P. Lucht

The project objective is to investigate the interactions among chemical species, temperature, and fluid motion as they relate to the formation of soot in flames. Local soot-formation rates have been determined at 0.1 to 0.2 MPa using laser-velocimetry flow-field measurements and light-scattering measurements of soot size and number density. Laminar axisymmetric ethylene-air diffusion flames have been studied at pressures up to 1.0 MPa to examine how the balance between soot formation and oxidation processes changes with pressure. The quantity of soot that is formed in the early regions of these flames increases with pressure, and the extent of soot removal by oxidation decreases

with pressure. Soot particle temperatures start to decrease late in the soot-formation region, removal of soot by oxidation ceasing when the particle temperature drops below about 1400 K. Turbulent jet diffusion flames have been examined at pressures up to 0.8 MPa to investigate the effect of turbulent mixing on soot formation. Peak time-averaged soot volume fractions are found on the centerline in these flames, unlike laminar coflowing flames where the peak soot concentration is located off-axis, just inside the position of the flame front. At any position and at all pressures, the turbulent flames consist of alternate soot-laden and soot-free zones. At low pressures, the axial soot-volume-fraction profiles approach universal functions of normalized axial position for long characteristic flame residence time. At high pressures, lower soot-volume-fraction profiles are observed for increasing characteristic flame residence time. A counter-flow diffusion flame has been used to study the impact on soot formation of dilution of the fuel, preferential diffusion, and oxygen addition to the fuel. When the fuel is diluted with a fixed inert gas and flame temperature is held constant, the peak soot volume fraction varies in direct proportion to the initial fuel concentration. [2.0 FTE]

56. Turbulent Reacting Flow Research
R. Dibble, R. Schefer, R.P. Lucht, J.-Y. Chen

This research is directed toward an increased understanding of the coupling between the chemical kinetic and turbulent transport processes occurring in chemically reacting flows. The long-term goal is to use these data to improve predictive capabilities in turbulent combustion. A nonpremixed turbulent jet flame is investigated, using multispecies Raman concentration and temperature measurements and laser-induced fluorescence to determine simultaneously OH radical concentrations. Experimental measurements have been compared with model predictions of chemical nonequilibrium in the turbulent jet flames. A Monte Carlo probability function (pdf) approach that incorporates reduced chemical reaction mechanisms is used to model these parabolic reacting flows. The structure of the turbulent flame zone in lifted and bluff-body diffusion flames has also been investigated using simultaneous two-dimensional imaging of the CH radical and CH₄. Experimental data have been compared with the predictions of flamelet and dissipative eddy models. Scalar dissipation levels and the effects of heat release on turbulence properties in the flow are determined from images of CH₄ concentrations. For the bluff-body flow, the experimental data are compared with a large-scale eddy simulation model of the flow. [3.0 FTE]

57. Flame Chemistry: Modeling and Experiments
G.A. Fisk, J.A. Miller, R.J. Kee, J.L. Durant

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 the formation and destruction of pollutants. Recent work on the flame chemistry of nitrogen-containing species contributed to the development of RAPRENO_x, a chemical process for removing nitrogen oxides from exhausts. Current emphasis is on the chemistry of carbon-containing species in rich oxygen/acetylene flames, particularly the reactions that form soot precursors such as diacetylene. Experiments conducted in a low-pressure flame give useful spatial resolution through the reaction zone. Laser diagnostics are used to determine temperature and the concentration profiles of radicals such as OH, CH, and CN. Mass-

spectrometric techniques yield 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. Careful comparison of modeling with experimental results, aided by sensitivity analysis, enables extension and validation of the reaction mechanisms that govern flames. In addition to studying steady-state flames, this research is developing computational techniques for treating ignition in combustible mixtures. The effects of temperature and pressure perturbations on the ignition process are areas of present emphasis. [4.0 FTE]

58. Chemical Kinetics and Dynamics
*G.A. Fisk, F.P. Tully, J.L. Durant,
D.W. Chandler, C. Melius, J.A. Miller,
E.A. Rohlfing*

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 hydrocarbons. Recent experiments have determined the rates at which OH abstracts primary, secondary, or tertiary hydrogen from alkanes. The results verify the intuitive concept that different sites in a molecule react independently, and are used extensively in modeling the chemistry that leads to knock in internal combustion engines. Fundamental studies of the kinetics of nitrogen-containing species recently led to the invention of RAPRENO_x, a chemical process that removes the oxides of nitrogen from exhausts. Theoretical approaches augment experiments. Quantum chemical calculations define the potential-energy surfaces on which chemical reactions occur. Statistical theoretical methods are then used to calculate the rates of important reactions in regimes for which experimental results are not available or are not consistent. Recent theoretical work has furthered the understanding of the OH + C₂H₂ and the O + C₂H₅ reactions. Studies of dynamics emphasize collecting quantum-state-resolved data for elementary processes such as intermolecular energy transfer and photodissociation. Results of recent studies on rotational relaxation in H₂ and in HCl have advanced the understanding of collision-induced energy transfer. Photofragment imaging, recently developed in this project, is a valuable technique for collecting highly resolved data on the dynamics of processes such as photodissociation. Initial results have demonstrated its use in studies of CD₃I and H₂S. [5.0 FTE]

59. Combustion Research Facility (CRF) Diagnostics Research: Coherent Raman Processes
*R.E. Palmer, R.L. Farrow, L.A. Rahn,
R.P. Lucht*

This project aims at developing coherent Raman diagnostic techniques in support of CRF programs. Detailed studies are made of the significance of several processes affecting CARS, a leading technique for time-resolved measurements of temperature and major species concentrations. Processes studied recently include collisional broadening, Doppler broadening and narrowing, pump laser photon statistics, laser line shape convolutions, and collisional narrowing of the Q branch. A high-resolution CARS system is used to examine saturation (another consideration when analyzing CARS measurements), to perform pump-probe experiments for measuring inelastic rota-

tional state-to-state transfer rates directly, 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 data base of spectral parameters for important combustion species such as nitrogen, carbon monoxide, hydrogen, and water vapor. This project is supported through KC-03-01-04-0. [5.0 FTE]

60. Combustion Research Facility (CRF) Diagnostics Research: Advanced Methods
R.E. Palmer, J.E. Goldsmith, M.L. Koszykowski, A.M.F. Lau, F.P. Trebino

This project supports development and theoretical understanding of new nonlinear laser-based techniques for detecting trace species and collision-induced processes in combustion environments. Profiles of hydrogen atoms in hydrogen/oxygen and hydrocarbon flames have been obtained. Photochemical effects in measurements of hydrogen and oxygen atoms in flames have been observed. Detailed studies of Doppler-free spectra of OH and CO have been made. Collision-induced resonances, involving nonlinear mixing of up to fourteen photons, for transitions between hyperfine and Zeeman states in sodium aspirated into flames, have been detected. In the area of theoretical studies, collisional narrowing of nitrogen and CO are modeled both by semiclassical scattering calculations and by simple scaling theories based on fits to experimental data. Hydrogen linewidths are modeled with similar scaling theories. Models have been developed to predict Doppler-broadened saturated line shapes (both transient and steady-state), and pump laser photo statistics. A new perturbation expansion and diagrammatic technique have been developed to interpret collision-induced high-order resonances. This project is supported through KC-03-01-04-0. [4.0 FTE]

Atomic Physics

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Physics Division \$1,583,000

61. Beam-Foil and Ion-Beam Laser Interactions
H.G. Berry, L. Young

Resonant laser excitation is used to study molecular and atomic ion structures. High spectral resolution is achieved by collinear excitation of fast ion beams with CW narrow-frequency laser beams and the use of rf/laser double-resonance techniques. Work on molecular ions is aimed at achieving understanding of both electronic and geometrical structures of simple systems. Several double-resonance techniques are under way to study hyperfine structures in N_2^+ and other simple molecular ions. *Ab initio* theoretical understanding of hyperfine structure in metallic and rare-earth ions is being tested. Other studies include fundamental problems of relativistic quantum mechanics and QED in few-electron systems. New double-

resonance measurements are in progress for all these systems. Some collision studies of fast ions in solids and gases are continuing. [4.7 FTE]

62. High-Resolution Laser-RF Spectroscopy with Atomic and Molecular Beams
W.J. Childs

This project is directed toward increasing understanding of the structure of many-electron atoms and diatomic molecular radicals through high-resolution laser and radiofrequency studies of atomic and molecular beams. The most recent work on atoms has focused on testing the *ab initio* multiconfiguration Dirac-Fock (MCDF) theory with studies of the hyperfine structure (hfs) of the 5d and 6s electron shells in LaI. The work reveals the contribution of s-electron shells to hfs in which the MCDF theory is completely inadequate and must be improved. A new collinear laser-ion apparatus used to study hfs in $^{151,153}Eu^+$ achieved the narrowest resonance lines yet seen with ion beams. The novel design of the rf section of the apparatus is a significant advance, and the new features are now being incorporated into larger machines in this country and in Europe. Systematic studies of the hfs and spin-rotation interactions in the related radicals LaO, YO, and ScO show perturbations because of very low-lying states not predicted by the best *ab initio* calculations. [1.1 FTE]

63. Atomic Physics at ATLAS
R.W. Dunford, H.G. Berry

The primary goal of the atomic physics project at ATLAS is to study atomic structure at a fundamental level. Recent experiments have included ultraviolet spectroscopy of two- and three-electron titanium and nickel, and measurement of the two-photon decay rate of the 2^1S_0 level in heliumlike nickel. Plans are under way for precision x-ray spectroscopy of one- and two-electron calcium, ultraviolet spectroscopy of two-electron bromine, and measurement of the two-photon decay rate of one-electron nickel. Exploratory work was performed using an ECR ion source that is to be part of the ATLAS accelerator but is available to this project temporarily. [3.2 FTE]

64. Interactions of Fast Atomic and Molecular Ions with Solid and Gaseous Targets
E.P. Kanter, Z. Vager

Argonne National Laboratory's 4.5-MV Dynamitron accelerator is used to study the interactions of fast (MeV) molecular ions with matter. The main objective is 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. This feature is that each molecular ion incident on a solid target forms a tight cluster of atomic ions that remain correlated in space and time as they penetrate the target. A unique apparatus has been developed that permits three-dimensional imaging of the trajectories of fragment ions resulting from the collisional dissociation of fast molecular beams. The new multiparticle imaging detectors developed for this work have exceptionally high resolution ($\sim .005^\circ$ and ~ 600 psec) in angle and time-of-flight and allow detection of multiparticle events consisting of up to 8 particles. The use of this detector system, combined with ultrathin stripping films and low-excitation ion sources, has allowed the direct determination of the geometrical structures of the molecular ions entering the target. These experiments have provided the

first direct measure of the nuclear densities within several small molecular and cluster ions. [4.8 FTE]

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Department of Applied Science **\$258,000**

65. Atomic Physics Research
K.W. Jones, B.M. Johnson

Studies of the physics of multiply charged heavy ions use synchrotron radiation from the Brookhaven National Synchrotron Light Source (NSLS). An x-ray beam line was improved by the addition of a 1:1 focusing mirror to increase the flux of white radiation delivered to the target by three orders of magnitude. A conversion to ultrahigh vacuum operation is under way so that windowless experiments can be done, resulting in an even greater flux increase compared to the original values. Monoenergetic radiation can be obtained by use of a monochromator in the experimental hut, but it will not be operated in the windowless mode initially. Experiments to study photoionization of ions using traps were initiated. The beam-line changes made during the NSLS x-ray ring shutdown will make possible better signal-to-noise ratios and greatly enhance the quality of the data. The first experiments used argon gas and ion beam targets. [2.2 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Materials and Chemical Sciences Division **\$355,000**

66. High-Energy Atomic Physics
H.A. Gould

The goals of this project are to understand atomic collisions of relativistic ions and to test quantum electrodynamics (QED) in very high atomic number (Z) atoms. These are new areas of research that involve physics not accessible at lower energies or with ions of lower atomic number. This research is conducted at the Lawrence Berkeley Laboratory's Bevalac, the world's only relativistic heavy ion accelerator. Recent results include measurements of the cross sections for multiple ionization of relativistic uranium ions and the channeling of relativistic uranium through silicon single crystals. These and earlier experiments have led to an understanding of relativistic heavy-ion-atom collisions, which in most cases is now more complete than for nonrelativistic collisions. Present activities include: (1) measurement of electron impact ionization cross sections for few-electron uranium, (2) measurement of a state-dependent capture cross section for one-electron uranium, and (3) a precision (0.1%) measurement of the Lamb shift in uranium. Future experiments will attempt to measure polarization in relativistic heavy-ion collisions and a new electron-capture mechanism in ultrarelativistic ion-atom collisions. [2.5 FTE]

67. Atomic Physics
M.H. Prior

This project uses the intense multiply charged ion beams available from the LBL ECR (Electron Cyclotron Resonance) ion

source for studies of atomic structure, collision dynamics, and radiative processes. Emphasis is on topics that have relevance to applied areas, such as CTR plasma diagnostics and advanced laser concepts, and/or that strongly challenge the current state of atomic theory, requiring the unique capabilities of the ECR source. Presently, efforts are under way that (1) yield metastable energy level structure of highly charged ions; (2) reveal details of multiple electron transfer processes, Auger electron, and x-ray emission spectra from ion-atom collisions; and (3) determine cross-sections for excitation of multiply charged ion states by electron impact. The latter studies are collaborative efforts with groups from other laboratories. [2.7 FTE]

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Physics Division **\$1,430,000**

68. Theoretical Atomic Physics at Oak Ridge National Laboratory (ORNL)
R.L. Becker, C. Bottcher

Theoretical predictions, interpretations of experimental results, and detailed calculations are made for atomic collision, radiation, and structure phenomena. Emphasis is placed on reactions of highly stripped ions with atoms, particularly those reactions of importance in fusion energy devices and those studied in atomic high-energy accelerator physics laboratories. Atomic excitation, ionization, and electron transfer (capture) are treated. Particular topics treated recently include coincident ionization and excitation of lithiumlike ions, a quantum scattering theory of electron-impact ionization of hydrogenic ions, single- and double-K shell vacancy production, and outer shell processes with multielectron projectiles. There is a major collaboration with the nuclear theory group at Oak Ridge National Laboratory to develop highly efficient algorithms to conduct numerical solutions of systems in the strong fields produced in collisions of highly charged ions at relativistic speeds, in particular the production of lepton pairs, i.e., (e^+e^-), ($\tau^+\tau^-$), and (u^+u^-). The exact numerical solutions of the three-body ion-atom scattering system are studied. The "constraint dynamics" methods of Dirac are being applied to study the structure of the e^+e^- system at very short distances. Theoretical approaches include the one-and-a-half center version of coupled-channels theory, the unification of shakeoff theory with collision theory, and the use of basis spline and collocation methods in the numerical integration of time-dependent quantal equations such as the time-dependent Hartree-Fock theory. [1.0 FTE]

69. Accelerator Atomic Physics
S. Datz, P.F. Dittner, C.R. Vane

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 Holifield Heavy Ion Research Facility (HHIRF). Electron capture, ionization, and transfer ionization (TI) have been studied for 0.1 to 1.0 MeV/nucleon highly charged ions colliding with helium. Single and double charge transfer cross sections have been measured. Zero-degree electron spectroscopy has been studied in coincidence with transfer ionization, and vacuum ultraviolet photons have been detected in coincidence with capture and with TI. These measurements indicate charge

transfer to lower n states with TI than with single capture, in qualitative accord with theory based on level transfer. Dielectronic recombination has been measured for boronlike ions, N^{2+} , O^{3+} , and F^{4+} . Correlated inelasticity and impact parameter dependence for 10 MeV carbon ions incident on neon and argon have been measured as a function of recoil ion charge state for various combinations of ingoing and outgoing charge state of the carbon ions. Energy resolution of 1.2 keV and simultaneous angular resolution of 0.005° were achieved using the Elbek magnetic spectrograph. Experiments are conducted to test the extent to which the electrons contained in a crystal channel can be quantitatively treated as a dense electron gas target. Beams of S^{15+} through silicon crystals are channeled at energies below and proceeding through thresholds for $n = 1 \rightarrow n = 3$ excitation. Since excitation cross sections rise sharply at threshold, the energy width of the excitation function should reflect the Compton profile of the electrons in the channel. [5.0 FTE]

70. EN Tandem Operations
P.F. Dittner

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, universities, and industry. Terminal voltages up to 6.5 MV are routinely available, and ion sources are sufficiently versatile to provide beams of (1) all ions from protons through fluorine and silicon through chlorine; and (2) many heavier ions including nickel, iodine, gold, and uranium. A VAX-750/CAMAC-based data acquisition system and the Elbek magnetic spectrograph 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, ion channeling through silicon crystals, dielectronic recombination rate measurements for boronlike ions, convoy electron studies, and zero-degree Auger electron spectroscopy of highly charged ions. [2.2 FTE]

71. Collisions of Low-Energy Multiply Charged Ions
R.A. Phaneuf, F.W. Meyer, C.C. Havener

Experimental studies of interactions of multiply charged ions with neutral atoms, molecules, and solid surfaces are performed at kinetic energies ranging from less than 1 eV/amu to several keV/amu. In this energy range, the electronic potential energy of the reactants is an appreciable fraction of the total interaction energy, and inelastic collision cross sections depend strongly on the electronic structure of the colliding systems. Studies of such processes yield important information about collision mechanisms and quasi-molecular structure, providing tests of developing theoretical models. An ion-atom merged-beams apparatus has been developed for use in conjunction with the ORNL-ECR multicharged ion source to measure absolute total electron-capture cross sections from keV/amu down to 1 eV/amu relative energy. Recently completed measurements for O^{5+} , N^{5+} , N^{4+} , and N^{3+} colliding with H or D atoms demonstrate the effects of ion-induced-dipole attraction between the reactants. Exploratory studies have also been made of the neutralization of multiply charged ions in grazing collisions with a solid surface at keV energies. Measurements of the energies of ejected electrons show the first evidence for the transfer of

electrons directly from inner shells of the solid to inner shells of the projectile ion. [1.2 FTE]

Sandia National Laboratories
Albuquerque, New Mexico 87185

Laser and Physical Chemistry **\$160,000**
Department-1124

72. Atomic Processes
A.V. Smith

The goal of this project is the development of efficient sources of coherent vacuum ultraviolet light via resonant frequency mixing. Atomic parameters for mercury have been measured, enabling the numerical modeling of mixing behavior in mercury vapor with good accuracy. In particular, 5% efficiency for the oxygen resonance wavelength of 130.2 nm is predicted. This prediction is being tested currently in a separate project. The possibility of using the light near 130 nm for photolithography and as the source for mixing deeper into the ultraviolet in another stage of frequency mixing is being explored. A second goal of this project is to measure (1) positions, shapes, and strengths of even parity autoionizing states of atomic oxygen and (2) the oscillator strengths of certain bound-bound transitions. These measurements should anchor future calculations of oxygen atomic structure, and they are also of importance for some SDI applications. [1.0 FTE]

Chemical Energy

Ames Laboratory
Iowa State University
Ames, Iowa 50011

Processes and Techniques Program **\$1,163,000**

73. Organometallic Complexes in Homogeneous Catalysis
R.J. Angelici

The general goal of this project is to understand how transition metal catalysts adsorb and activate molecules in various catalytic reactions. Current studies are directed toward understanding hydrodesulfurization of thiophenes on heterogeneous catalysts. Evidence for the π -adsorption of thiophene to the catalyst surface comes from the very similar patterns of deuterium exchange of thiophene on HDS catalysts and of π -thiophene in $(\eta-C_5H_5)Ru(\eta-C_4H_4S)^+$. The π -thiophene ligand in the latter complex is also activated to react with metal hydride sources which may be present on catalyst surfaces. These reactions lead to partially hydrogenated dihydrothiophenes which have been shown to eliminate sulfur and give desulfurized hydrocarbons. Thus, the dihydrothiophenes are key intermediates on the pathway to desulfurized products. They also react with transition metal cluster hydrides to give complexes which account for by-products in the HDS reactions. These reactivity studies provide a basis for understanding details of the mechanism for thiophene hydrodesulfurization. [2.3 FTE]

74. Chemical Kinetics and Reactivity of Transition Metal Complexes
J.H. Espenson

The objective of this work is to explore the mechanisms of chemical reactions related to DOE objectives in areas like homogeneous catalysis and synthetic fuels. Reactions of interest include the formation and cleavage of metal-carbon bonds, particularly metal alkyls. This includes spontaneous or solvolytic reactions such as heterolysis and homolysis of metal-carbon bonds. Also included are reactions in which other reagents attack the metal alkyl as in their reactions with electrophiles and radicals. Reactions of alkyl radicals with transition metal complexes are also being explored. This work relies on the generation of the radical, usually from an organometallic precursor by the use of laser flash photolysis, with the reactions of interest being monitored by coupling the radical reaction of interest to one involving large changes in the absorption spectrum. [3.7 FTE]

75. Multiple Pulse NMR Studies: Catalysis and the Chemical Constitution of Coal
B.C. Gerstein

Nuclear spin dynamics in the solid state 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 re-forming; (2) the use of NMR of quadrupolar nuclei such as ^{27}Al and ^{65}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; and (3) use of dipolar oscillation NMR to determine internuclear distances in unstable organic molecules trapped in frozen matrices at 80 K. [2.9 FTE]

76. Fundamental Investigations of Supported Bimetallic Catalysts
T.S. King

This project focuses primarily on supported, mono- and bimetallic catalysts with the intent of understanding how the chemical and structural properties of the highly dispersed transition metals affect catalytic performance. The parameters of most interest in this project are: (1) the abundance and morphology of surface atoms, (2) the relative surface composition of the various metals present, (3) the influence of promoters and poisons, and (4) the nature of adsorbed species. Solid-state NMR of ^1H , ^{13}C , ^{63}Cu , ^{65}Cu , ^{195}Pt , ^{133}Cs , and various other nuclei is used to investigate these parameters, in combination with more traditional catalytic and adsorption techniques. This approach allows determination of the state of metal atoms under reaction conditions, the structure of the adsorbed species, and the chemisorptive and reactive behavior of model reactants. [2.5 FTE]

77. Spectroscopic and Kinetic Characterization of Metal Oxide and Sulfide Catalysts
G.L. Schrader

The goal of this research is to provide a fundamental understanding of the catalytic reactions, catalyst structures and composition, and surface properties associated with metal oxides and sulfides. The catalysts being examined are used in

selective oxidation and hydrodesulfurization. Specific applications include paraffin oxidation (oxidative coupling of methane) and the processing of coal-derived or residua by reduced molybdenum sulfides. A complement of experimental approaches is used involving reaction engineering kinetic measurements and extensive catalyst characterization. *In situ* spectroscopic techniques, such as laser Raman and Fourier transform infrared spectroscopy, are used extensively to examine functioning catalysts. In particular, simultaneous spectroscopic and kinetic measurements are performed at the elevated temperatures and pressures more typical of industrial operating conditions. New techniques such as solid-state NMR also have important applications in the current research to identify active components and active sites for catalysts. The purpose of the experimental project is to provide fundamental relationships between catalyst structure, composition, and surface properties and catalytic activity and selectivity. [2.9 FTE]

78. High-Temperature Gas-Phase Pyrolysis of Organic Compounds
W.S. Trahanovsky

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 under study include their self reactions (oligomerization and polymerization), reaction with other species, and reactions in which they are transient intermediates. The experimental 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. Specific reactive molecules under study include *ortho*-quinodimethanes derived from benzene, naphthalene, phenanthrene, furan, and thiophene. A flow NMR technique has been developed which allowed the ^1H NMR spectra of some very reactive *ortho*-quinodimethanes to be obtained for the first time. Techniques required to obtain the NMR spectra of reactive molecules isolated in solid matrices at low temperature are under development. [2.0 FTE]

Argonne National Laboratory
Argonne, Illinois 60439

Chemical Technology Division

\$586,000

79. Fluid Catalysis
J.W. Rathke, M.J. Chen, R.J. Klingler

This research explores mechanisms of catalytic reactions that occur under forcing conditions of temperature and pressure. Currently under investigation are nucleophilic hydrogen activation processes that occur in the presence of soluble oxide complexes. Recent results indicate that the new oxide chemistry for methanol synthesis is adaptable to other homogeneous processes, including water-gas shifting, the hydrogenation of unactivated olefins, and, perhaps, even to the hydrogenation of nitrogen. Also explored are synthetic methods designed to incorporate shaped regions into stable phthalocyanine catalysts for

homogeneous reactions that occur at high temperatures and pressures. Alternative techniques for adapting multinuclear NMR spectroscopy to high pressure kinetic studies are also studied. The new chemistry is investigated using a combination of kinetic and spectroscopic techniques in addition to theoretical (molecular orbital) methods. [6.0 FTE]

Chemistry Division **\$2,119,000**

80. Inorganic/Fluorine Chemistry
E.H. Appelman

This project is directed toward (1) the synthesis and characterization of novel oxidants and fluorinating agents, (2) the elucidation of the mechanisms of their chemical reactions, and (3) the development of applications of such compounds as synthetic and analytical reagents. Materials of this type under current study include seven-valent neptunium ions in aqueous solution and the fundamentally significant molecule hypofluorous acid, HOF. A precise method for determining the oxygen content of high-temperature mixed-oxide superconductors has been developed. Future research will include studies of the interaction of reactive fluorine compounds with actinide ions in aqueous solution and investigation of the reactions of powerful electrophilic fluorinating agents with organic compounds. [1.4 FTE]

81. Premium Coal Sample Program
K.S. Vorres

This project provides the basic coal science community with the most pure samples available of eight U.S. coals. They have been collected, processed, and packaged to provide the coal in a form as much like the original coal in the seam as possible. Orders are filled for ampoules of either 10 grams of -20 or 5 grams of -100 mesh material. The nitrogen-filled ampoules are monitored for stability through measurements of the gas atmosphere and plasticity of the bituminous samples. A sufficient quantity has been prepared that the existing supply (including reserve material kept in 5 gallon carboys) should meet the demand for at least one decade. Analytical information is supplied to the users, and the amount reported is expanded as additional information becomes available. Symposia on "Research with Argonne Premium Coal Samples" have been organized through the Fuel Chemistry Division of the American Chemical Society. Over 170 orders for at least 6,000 ampoules have been filled from more than 102 requesting individuals or groups. [0.8 FTE]

82. Separation of Coal Macerals
R.E. Winans, G.R. Dyrkacz, C.A.A. Bloomquist

This project seeks to reduce the heterogeneity of coals by developing new methods for separating and characterizing coal macerals. The project focuses on (1) developing and utilizing combined two-dimensional chemical modification and density gradient centrifugation separations to achieve the ultimate separation of macerals; and (2) developing large-scale flow-separation systems using both centrifugation and magnetohydrostatic separations. [3.1 FTE]

83. Characterization and Reactivity of Coals and Coal Macerals
*R.E. Winans, R. Hayatsu, R.E. Botto,
 R.G. Scott, R.L. McBeth*

The major objective of this project is to elucidate the chemical and physical structures of the Argonne Premium Coal Samples

and their separated coal maceral constituents. Data obtained in this project will be used to better understand the chemical, thermal, and biological reactivity of these materials. The goals are being realized through selective chemical modification and solubilization procedures, coupled with multiple instrumental characterization. Also, coal model systems are both chemically synthesized and developed. These models include synthetic coal formed from presumed bioprecursors and clays, polymers, and large molecules. Coal macromolecules are investigated by multinuclear solid NMR, pyrolysis high-resolution mass spectrometry, and fast atom bombardment HRMS. Physical structure is studied by small-angle neutron scattering and NMR. The understanding of coal obtained in this study should help to predict coal reactivity, which could lead to the development of more efficient and clean methods to use coals. [9.3 FTE]

84. Stability of Premium Coal Samples
R.E. Winans, P.H. Neill, K.S. Vorres

The project objective is to develop techniques to examine any chemical or physical changes that may occur in the Argonne Premium Coal Samples. The study is also providing new, fundamental information on this unique set of coal samples. For the first time, inverse gas chromatography (IGC) is being used to examine changes (upon heating) in the properties of coals. The results from IGC are being correlated with high-temperature small-angle neutron scattering data. Solvent extraction of the coals and subsequent separation and characterization of the extracts are being done in a quantitative systematic manner. [1.0 FTE]

Brookhaven National Laboratory
Upton, Long Island, New York 11973

Department of Applied Science **\$728,000**

85. High-Temperature Chemistry
J.J. Egan

This project studies the thermodynamic, transport, and electronic properties of liquid and solid compound semiconductors as well as metal-molten salt systems at high temperatures. Electrochemical and calorimetric techniques are being used to explore and characterize these systems. Special galvanic cells with solid electrolytes are employed to examine alloy systems in both the liquid and solid state. A high-temperature twin Calvet type calorimeter is also operated to study ionic alloys, which are liquid semiconductors. Results yield the concentration and mobility of electrons and electron holes in these systems. The electronic conductivity of molten salts is being examined by special polarization techniques, because the conductivity property is so important in determining the efficiency of electrolysis in the production of metals and the self-discharge of molten salt batteries. Coulometric titration methods are undertaken to study solid compound semiconductors. Results of all studies are explained in terms of appropriate atomic models. [3.2 FTE]

86. Metal Hydrides
J.J. Reilly

This project focuses on determining the thermodynamic properties, reaction kinetics, and crystal structures of compounds that contain interstitial hydrogen. A particular goal is to relate all pertinent data and hypotheses to develop a predictive capability

regarding the behavior of a given system. Current topics of interest are the properties of metal hydride suspensions, the effect of the incorporation of hydrogen into superconducting oxides, crystal structure of metal hydride phases, and improved powder diffraction methods and structural refinement calculations. The experimental techniques and methods used are: (1) x-ray and neutron diffraction; (2) equilibrium pressure-temperature-composition measurements; and (3) a high-pressure apparatus to study the kinetics of the formation and decomposition of metal hydrides in liquid suspension. [3.8 FTE]

Chemistry Department**\$629,000****87. Organometallics in Homogeneous Catalysis***R.M. Bullock, M.A. Andrews*

Experimental studies form the basis for investigations into fundamental aspects of organometallic chemistry and homogeneous catalysis. Current endeavors seek to discover new catalytic transformations targeted at biomass conversion and to probe mechanistic aspects of transition metal hydride catalyst systems. Carbohydrates have rarely served as substrates in homogeneous transition metal catalysis, despite their great natural abundance and rich chemical functionality. Reactions are being conducted to test new strategies for using organometallic complexes to convert sugars and other typical biomass components into useful energy and chemical feedstock compounds such as carbon monoxide and hydrogen. A number of experimental difficulties in this interdisciplinary area have been resolved and significant preliminary results secured, demonstrating the sequential, multiple dehydrogenation and decarbonylation of sugar alcohols. Transition metal hydride catalysts function by delivering hydrogen as a proton (H^+) hydride (H^-), hydrogen radical ($H\cdot$), or hydrogen molecule (H_2) to organic substrates. Synthetic, kinetic, and mechanistic experiments are conducted to distinguish among these reaction modes, with an emphasis on complexes that provide meaningful models for intermediates in the hydrogenation and hydroformylation of alkenes. Strong new evidence has been obtained for the participation of radical pathways and aldehyde complexes in these reactions, together with quantitative data for rates of H-atom transfer. [5.0 FTE]

88. Molecular Structure and Chemical Reactivity on Surfaces*J. Hrbek*

The main objective is to develop and improve the understanding of molecular processes at the gas-solid interface, with emphasis on catalytically important systems. Focus is on the electronic and geometric effects of surface modifiers, such as alkali metals, electronegative elements, and second metals, on the coadsorbed molecules. Coadsorption of alkali metals and oxygen is studied in mono- and multilayer coverage ranges. Dissociatively adsorbed oxygen is found to stabilize thermally alkali metal overlayers. A new oxygen species with an O 1s binding energy above 532 eV was observed in the K-O and Cs-O systems, together with several intense O 2p levels in the valence band region of photoemission spectra, indicating the formation of peroxy and superoxy species. All alkali metals studied (lithium, sodium, potassium, and cesium) show a negative binding energy shift of core levels upon oxidation, suggesting unusual electronic interactions in the surface complex. Currently, modified surfaces containing an alkali metal complex with weakly bonded

oxygen are used in the oxidation studies of carbon monoxide and ethylene. This project uses an array of surface techniques, including photoemission spectroscopy, Auger spectroscopy, thermal desorption spectroscopy, vibrational spectroscopy, and electron diffraction and synchrotron radiation spectroscopies. [2.0 FTE]

**Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720****Applied Science Division****\$200,000****89. Homogeneous Catalytic Hydrogenation of Polynuclear Heteroaromatic Nitrogen Compounds***R.H. Fish*

The fundamental aspects of the reactions of polynuclear heteroaromatic nitrogen compounds (an important class of model coal compounds) with rhodium, ruthenium, and other metal complexes are being studied. These studies include the mode of bonding of the nitrogen compounds to the metal centers (i.e., N- versus π -bonding) and use of rhodium, ruthenium, and other metal complexes and their precursors as catalysts in the regioselective nitrogen heterocyclic ring hydrogenation reaction. Also planned is definition of the mechanism of this selective hydrogenation reaction by studying relative rates, intermediate hydride formation, transfer of hydrogen to nitrogen substrate, inhibition and enhancement of the relative rates of nitrogen ring reduction, comparison of the homogeneous to heterogenized homogeneous catalysts in regard to relative rates and mechanism, and the role of N- versus π -bonding in the overall selective hydrogenation reaction. Recent results with pentamethylcyclopentadienylrhodium dication (Cp^*Rh^{2+}) and several heteroaromatic nitrogen compounds, such as quinoline, isoquinoline, 1,2,3,4-tetrahydroquinoline, 2-methylquinoline, N-methylindole, and N-methylpyrrole, clearly indicated that N- versus π -bonding depends on the structure of the nitrogen ligand and the availability of nonbonding electrons on the nitrogen atom. In addition, the N-bonded $Cp^*Rh(quinoline)_x^{2+}$ complex and two of its precursors, $Cp^*Rh(p\text{-xylene})^{2+}$ and $Cp^*Rh(acetone)_3^{2+}$, have been shown to be excellent catalysts in the regioselective hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline. [1.5 FTE]

Materials and Chemical Sciences Division **\$1,022,000****90. High-Energy Oxidizers and Delocalized-Electron Solids***N. Bartlett*

The main aim of this project is the synthesis and characterization of new materials that may have value in electrochemical applications or in the efficient conversion of light to electrical energy. The synthetic work tests models and theories that correlate physical properties (such as electrical conductivity) with chemical composition and structure. Major aims in the synthetic strategies are (1) to tailor-make the band gap in semiconductor materials and (2) to achieve high carrier concentration and mobility in the conductive materials. Present emphasis is on two-dimensional networks, such as those related to graphite. Electron oxidation of such materials (with accompanying intercalation to form salts) generates durable and conductive

materials (some conducting better than aluminum). The layered materials can often be oxidized (and intercalated) electrochemically in reversible processes and some may find use in high-energy electrodes. Physical and chemical studies are being applied to such materials to determine the structure and bonding changes that accompany oxidation and reduction. Salts that are either proton conductors or fluoride-ion conductors, and that are resistant to oxidation but are not metallic, are being sought as solid electrolytes for use with the metallic-layer-material salts. [4.5 FTE]

91. Catalytic Hydrogenation of Carbon Monoxide
A.T. Bell

The purpose of this project is to develop an understanding of the fundamental processes involved in catalytic conversion of carbon monoxide and hydrogen to gaseous and liquid fuels. Focus is on defining the factors that limit catalyst activity, selectivity, and resistance to poisoning, and the relationship between catalyst composition/structure and performance. Surface diagnostic techniques (LEED, AES, XPS, EELS, NMR, IRS, TPD) 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. [6.0 FTE]

92. Transition Metal Catalyzed Conversion of CO, NO, H₂, and Organic Molecules to Fuels and Petrochemicals
R.G. Bergman

The goals of this project are the development of new chemical reactions in which transition metals interact with organic materials, and the understanding of how these reactions work. A recent discovery on this project was the finding that certain hydrido-iridium and -rhodium complexes undergo oxidative addition into the carbon-hydrogen bonds of completely saturated hydrocarbons ($M + R-H \rightarrow R-M-H$). Since this finding was the first example of this long-sought alkane C-H activation reaction, research is now being directed at examining the scope, selectivity, and mechanism of the process. During the current year, extensive mechanistic studies were conducted on the first rhodium-based alkane activation system. In this work, strong evidence was obtained that a weak alkane-metal complex is formed on the reaction pathway leading to the final C-H inserted product. In addition, the first quantitative metal-hydrogen and metal-carbon bond dissociation energies were determined for the iridium C-H activating system. These results demonstrated that insertion of iridium into the C-H bonds of alkanes is very exothermic; an even more powerful thermodynamic driving force exists for insertion of the metal into the C-H bonds of arenes. [4.0 FTE]

93. Formation of Oxyacids of Sulfur from SO₂
R.E. Connick

The primary focus of the research is the fundamental chemistry of sulfur species formed from sulfur dioxide in aqueous solution and the reactions of these species. The chemistry of these species is of particular importance in the problems associated with atmospheric pollution by sulfur dioxide and the resulting formation of acid rain. One of the most important reactions is the

oxidation of S(IV) by oxygen in aqueous solution because this reaction plays a key role in both wet flue-gas desulfurization processes and in the formation of acid rain in aquated aerosols. Work has been concentrated on the latter project but additional oxidation-reduction chemistry of S(IV) should be investigated, particularly reactions involving two or more oxidation states, (e.g., reactions involving HSO₃⁻, H₂S, S₈, and the polythionates). A secondary goal is to determine factors controlling the rate of substitution reactions in the first coordination sphere of metal ions. Computer modeling has been extended to three dimensions. Interesting preliminary results are being obtained for configurations of the activated complex. [1.5 FTE]

94. Synthetic and Physical Chemistry
W.L. Jolly

The objective of the photoelectron spectroscopic part of this project (which has been concluded) was to determine the nature of the chemical bonding in transition metal organometallic complexes related to catalytic systems. The experimental tool is gas-phase x-ray photoelectron spectroscopy, which provides atomic core electron-binding energies. The binding energies give information about the distribution of valence electron density and the nature of the chemical bonding in the molecules. By measuring the core binding energies of appropriate transition metal compounds, it is possible to study the interaction of metal d electrons with various ligands, such as organic groups, carbonyl groups, and nitrosyl groups. One can identify and distinguish various modes of ligand-metal bonding that have analogs in the molecules chemisorbed on metal surfaces and in the intermediates of catalyzed organic reactions. The objective of the synthetic part of this project is to prepare compounds of novel composition and structure using electric discharges and ultraviolet photolysis. Unstable molecular fragments can be generated in low-pressure gas flow systems using electric discharges or ultraviolet irradiation. These can be either quenched or allowed to react with other molecules, with formation of unusual products. The technique will be applied to organometallic systems and nonmetal compounds. [1.0 FTE]

95. Potentially Catalytic and Conducting Oligo-Organometallics
K.P.C. Vollhardt

The purpose of this program is to combine synthetic organic and organometallic methodology in the construction of novel organometallic materials with potential in catalysis and materials science. In particular, iterative approaches to the synthesis of linked cyclopentadienyl ligands are being studied. Subsequent attachment of a variety of metal centers with control of their binding sequence is giving rise to linear and angular oligometallic arrays in which the metals are held in an unnatural configuration. Such materials hold promise in potential applications as catalysts in a variety of processes of current fundamental and industrial interest, such as coal hydrogenation and conversion to liquid fuels, small molecule activation, new reaction chemistry, photocatalysis, and photochemical energy storage, water splitting, and others. Moreover, the methods to be developed are anticipated to provide access to structures containing alternating organic and metallic layers with potential conducting behavior. Results should provide unique catalytic and potentially conducting materials. [3.5 FTE]

Los Alamos National Laboratory
Los Alamos, New Mexico 87545**Isotope and Nuclear Chemistry Division** **\$356,000****96. Transition Metal Mediated Reactions of SO₂**
G.J. Kubas, R.R. Ryan

This research has focused on the basic chemistry of energy-related small molecules, primarily SO₂ and H₂, emphasizing activation of S=O and H-H bonds by transition metal complexes. A fundamental understanding of the cleavage of these bonds will benefit efforts to control SO₂ emissions, providing new directions in metal-catalyzed reactions. Homogeneous catalytic reduction of SO₂ to sulfur and H₂O by hydrogen on organometallic molybdenum sulfide complexes has been achieved and mechanistic studies are under way. SO₂ has been found to undergo oxygen transfer reactions that may be relevant to the catalytic cycle. Disproportionation of SO₂ to sulfur and SO₃ (as SSO₃ or SO₃H ligands) occurs on reaction with Cp'₂Mo₂S₄ and Cp'₂Ru(CO)₂H (Cp' = C₅Me₅). Thiosulfate ligands such as those in the products Cp'₂Mo₂S₃(μ-SSO₃) and [Cp'₂Ru(CO)₂]₂(μ-SSO₃) have now been observed to be formed from SO₂ in several systems and may possess important chemistry. SO₃ can be readily stripped off the Mo-SSO₃ complex with weak bases to regenerate starting complex, possibly leading to a catalytic cycle where SO₂ is spontaneously converted to sulfur and sulfuric acid (from SO₃). In regard to H₂ activation, the discovery of side-on bonding of H₂ molecules to metals represents the first stable σ-bond complex and serves as a prototype for other σ-bond activations (e.g., C-H in hydrocarbons). Dihydrogen and other σ-bond complexes may be important in catalysis, and the reactivity of M-H₂ complexes is being studied. Thermodynamic, kinetic, isotopic exchange, and protonation studies are in progress to characterize dihydrogen-dihydride ligand equilibria, catalysis of H₂/D₂ mixtures to HD, and other H-H bond cleavage processes. [1.90 FTE]

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831**Chemical Technology Division** **\$540,000****97. Kinetics of Enzyme-Catalyzed Processes**
E. Greenbaum, J. Woodward

Key areas of progress were in the areas of (1) photochemical flash precipitation of catalytic platinum metal clusters; (2) electron transfer reactions at the photosynthetic membrane metal colloid interface; (3) bioelectronic materials; and (4) the demonstration of synergism among the components of the cellulase enzyme system. A new interfacial photochemical reaction at the photosynthetic membrane interface in which hexachloroplatinate is converted to metallic platinum is reported. The reductive precipitation of zero-valent platinum from a hexachloroplatinate ion requires four reducing equivalents. *In situ* photochemical reductive precipitation of hexachloroplatinate has been performed using the photochemical apparatus of isolated spinach chloroplasts illuminated with single-turnover, saturating flashes of lights. By continuously monitoring for the onset of photoevolved hydrogen, it is possible to set an upper limit for the minimum number of platinum atoms required to form catalytically active platinum. The key results of the experi-

ments are that (1) the onset of catalytic hydrogen evolution during the creation of platinum metal catalyst can be observed with 50 atoms or less and (2) a stable metal catalyst is created at about 500 atoms or less. Synergism between purified cellulase components cellobiohydrolases I and II has been studied and found to be greatest when cellulase was incubated with nonsaturating concentrations of these components. [4.0 FTE]

Chemistry Division **\$2,530,000****98. Organic Chemistry and the Chemistry of Fossil Fuels***A.C. Buchanan, P.F. Britt, L.L. Brown,
E.W. Hagan, R.R. Chambers*

This project is aimed at obtaining new molecular level knowledge of the organic chemical structure and reactivity of coals. Such fundamental information will be required for developing novel processes for liquid fuels and chemicals from coals. Diagnostic organic reactions are developed and used to identify and quantify specific structural features of coals. Derivatization of reaction centers with ¹³C and ¹⁴C double labeled reagents, solid-state ¹³C NMR, and parallel studies with model compounds are integral to this project. A series of indicator carbanion bases of well-defined strengths is being used to quantitatively investigate acidic C-H structures in bituminous coals, with emphasis on structures in the pK_a range of 12 to 33. The development of solid-state NMR techniques for studying coal structure is also being pursued. Current efforts focus on the development of a novel ¹H-¹³C-³¹P double cross polarization ¹³C-NMR technique that detects only those carbons within ca. 4.0 Å of a phosphorus atom. This methodology, when coupled with the selective chemical introduction of a phosphorus-containing moiety, permits a much more detailed assessment of localized structure in complex fossil fuels. Thermolysis studies of α,ω-diphenylalkanes covalently attached to a silica surface model the impact on thermal reaction pathways of restricted radical and substrate mobility, imposed in coals by the cross-linked macromolecular structure. The results provide new mechanistic insights into the thermal reactivity of coal, which underpins the processes of pyrolysis, liquefaction, and coking. [8.2 FTE]

99. Basic Aqueous Chemistry to High Temperatures and Pressures*R.E. Mesmer, H.F. Holmes, W.L. Marshall,
D.A. Palmer, J.M. Simonson*

The purpose of this project is to conduct experimental research on reactions and thermodynamic properties of important classes of solutes in water at high temperatures and pressures. Systems under study often have immediate applicability in energy-related technologies, but always form a basis for evaluating theoretical models that can advance understanding and predictability of chemical reactivity. Topics include thermodynamic properties of (single and mixed) electrolytes and nonelectrolytes in addition to equilibrium and kinetic studies providing enthalpies, volume changes, and equilibrium constants for reactions such as ion association, acid and base ionization, complexation, oxidation-reduction, hydrolysis, and solubility in aqueous solutions. New apparatus and techniques to complement existing capabilities are being continually developed for precise measurements. Experimental capabilities include flow calorimetry, isopiestic and electrochemical apparatus, electrical

conductivity, vibrating-tube densimetry, and Raman and ultra-violet-visible spectrophotometry for measurements to extremes of temperature and pressure. Results have application in steam generation, nuclear and chemical waste disposal, chemical processing, the extraction of heat and material resources, and basic hydrothermal geochemistry. New initiatives will involve structural information on electrolytes at high temperatures and pressures using neutron and x-ray scattering techniques. [4.9 FTE]

100. Heterogeneous Catalysis Related to Energy Systems

S.H. Overbury, D.R. Huntley, D.R. Mullins

This project involves the study of adsorption and reaction of molecules at well-characterized metal surfaces. Major research topics are surface catalyzed hydrodesulfurization reactions and the effects of adsorbates on surface structure and the bonding geometry of chemisorbed species. Ultrahigh vacuum techniques are used to prepare and maintain a single crystal surface in a desired state for exposure to various types of adsorbates, and for subsequent analysis. The techniques of high-resolution electron energy loss, thermal desorption, Auger electron, and x-ray photoemission spectroscopies have been applied to study adsorption of methanethiol on Ni(110) and to determine the kinetics of desulfurization. The effects of surface oxygen and sulfur atoms on the kinetics have been examined. The technique of low-energy ion scattering as a tool for determining surface structure has been applied to surfaces with atomic adsorbates. Recently, the structure of oxygen-covered W(001), the interaction of oxygen and carbon on W(001), the structure of ultrathin layers of copper on tungsten, and the structure of NiAl alloy surfaces have been analyzed. A project to use synchrotron radiation to study thermally induced changes in molecular chemisorption geometry and surface-adsorbate electronic structure is in early stages of development. [2.4 FTE]

101. Photolytic Transformations of Hazardous Organics in Multiphase Media

G.P. Smith, A.S. Dworkin, S.P. Zingg, R.M. Pagni

Project emphasis is changing from the chemistry of aromatic compounds in molten salt catalysts to a study of the photochemistry of aromatic compounds in water and sorbed on solids. Current molten salt research is directed at reactions in AlCl₃-EMIC melts (EMIC = 1-ethyl-3-methylimidazolium chloride), in particular: (1) reversible protonation of arenes by HCl in melts with >50 m/o AlCl₃ and (2) electrochemical reduction of arenes in melts with <50 m/o AlCl₃ to form persistent radical anions, and the oxidation of these arenes in melts with >50 m/o AlCl₃ to form persistent radical cations. Current photochemical research is an investigation of (1) the partitioning of polycyclic aromatic hydrocarbons (PAHs) between the solid and liquid phases of slurries and (2) the products formed from photoinduced reactions of PAHs in slurries, particularly under oxidizing conditions. In the future, the dynamics of selected examples of these photochemical reactions will be studied. Radical cations, which are key intermediates in many reactions of aromatics in molten salt catalysts, are suspected intermediates in photooxidations of PAHs in polar solvents. Much of the spectroscopic methodology used on the molten salt program to study these intermediates is applicable to the photochemistry program. [3.3 FTE]

**Pacific Northwest Laboratory
Richland, Washington 99352**

Chemical Sciences Department

\$579,000

102. Free-Radical Chemistry of Coal

J.A. Franz, M.S. Alnajjar, S.T. Autrey

The objective of this project is to establish a quantitative mechanistic description of radical ion and radical mediated molecular rearrangements and atom transfer reactions important to thermal degradation of coal. Efforts include determination of absolute rates of organic free-radical rearrangements, rate expressions for hydrogen atom transfer between sulfur-centered radicals and thiols, and absolute rate expressions for hydrogen atom transfer to carbon-centered radicals from CH, PH, MoH, SH, and other heteroatom donors, using radical clock and kinetic laser spectroscopic methods. Radical displacement reactions at sulfur and selenium by 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 hypervalent radical displacement potential surfaces, such as that for alkyl radical displacement at sulfur. A theoretical and experimental study of the process of inter- and intramolecular hydrogen transfer between aromatic rings (radical hydrogen transfer) is under way. Development of procedures for the quantitative application of ultrahigh speed magic angle spinning CPMAS NMR to coal structure determination is under investigation. [2.8 FTE]

103. Chemistry and Kinetics of Precursors of Coal

J.A. Franz, R.J. Miller, N.K. Sudeman

This project examines the structure and reactions of organic free radicals derived from saccharide, peptide, and lignin parent structures. The approach is to apply kinetic electron spin resonance spectroscopy, optical spectroscopic, and product study kinetic methods to examine radical and ionic rearrangement and fragmentation pathways involved in converting parent biological structures to vitrinite constituents. Efforts under way include (1) application of kinetic electron spin resonance spectroscopy for the observation of carbon skeletal rearrangements in selected saccharide, protein, and lignin structures, and (2) observation of dynamic processes in radical-radical reactions in hydrogen-bonded systems in aqueous and organic phases for structural assemblies which impose motional restriction on intermediate radicals and radical ions affecting the selectivities in carbon-carbon bond forming reactions. Rate expressions for radical β -scission reactions leading to cleavage of the lignin Ar-C₂O-Ar linkage are being developed. [1.2 FTE]

**Sandia National Laboratories
Albuquerque, New Mexico 87185**

Surface Science Division

\$386,000

104. Surface Catalytic Studies

D.W. Goodman

The goal of this research is to develop an understanding of the relationship between surface structure and catalytic activity/selectivity. 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, ultraviolet, and x-ray photoemission spectroscopy, temperature programmed desorption, low-energy electron diffraction, high-resolution electron energy loss spectroscopy, and Fourier transform infrared spectroscopy. Current focus is on: (1) the study of the unique catalytic properties of monolayer and submonolayer metal films of "active" catalytic metals (e.g., Ni, Ir, and Pt) on "inactive" substrates (e.g., W, Re, and Mo); (2) the investigation of methanation, ethane hydrogenolysis, and cyclohexane dehydrogenation of two-dimensional overlayers of Cu-Ni on W, with emphasis on the critical ensemble size requirements for each of these reactions; and (3) the simulation of small-particle catalysts, using corrugated single crystal surface. [2.0 FTE]

Solar Energy Research Institute Golden, Colorado 80401

Solar Fuels Research Division \$231,000

105. *Basic Research in Synthesis and Catalysis* D.L. DuBois, C.J. Curtis

This project involves the synthesis and characterization of new inorganic and organometallic complexes for evaluation as catalysts for reducing substrates such as CO₂ and CO to chemicals and fuels. A series of complexes of the type [Pd(triphosphine)(solvent)](BF₄)₂ have been found to catalyze the electrochemical reduction of CO₂ to CO. An ECEC mechanism appears to operate during the catalytic cycle. The solvated Pd(II) species is reduced to Pd(I) species which reacts rapidly with CO₂ to form a Pd(I)CO₂ complex. This intermediate is reduced to a Pd(O)CO₂ complex which is protonated to form CO and H₂O and to regenerate the solvated Pd(II) species. The mode of decomposition of these catalysts involves the formation of Pd(I) dimers. Work on CO reduction is being conducted in two areas. In the first area, dinuclear zirconium hydride complexes have been synthesized and shown to react stoichiometrically with CO to yield formaldehyde complexes. In the second area, studies aimed at developing catalysts for electrochemical CO reduction have been initiated. In this effort, reactions of electrochemically generated transition metal hydrides with electrophilic metal carbonyl complexes are being examined with the objective of observing and studying some of the fundamental steps that could lead to the development of a catalyst. [1.6 FTE]

Separations and Analysis

Ames Laboratory
Iowa State University
Ames, Iowa 50011

Processes and Techniques Program \$1,050,000

106. *Analytical Spectroscopy* V.A. Fassel, A.P. D'Silva

The current emphasis in this project is the development of novel spectroscopic excitation sources based on energy transfer from high-energy metastable ($\tau \geq 0.5$ msec) states of atomic and

molecular species to analyte species. Such excitation sources are being tailored for highly sensitive element-selective detection in gas, liquid, and supercritical fluid chromatography. For the analysis of aerosols and solids, atomic species generated in laser-produced microplasmas are allowed to interact with metastable species. In the inductively coupled plasma field the effort is focused on novel approaches such as high-speed cinematography, plasma diagnostics, and the compilation of a high-resolution spectral atlas of 71 elements. [2.3 FTE]

107. *Analytical Separations and Chemical Analysis* J.S. Fritz

Two new chromatographic methods have been devised for the determination of small amounts of water in analytical samples. One involves a novel acid-catalyzed spectrophotometric detection method for liquid chromatography. The other uses gas chromatography to separate the products of the reaction of water with 2,2'-dimethoxypropane. New eluents and greatly improved column packings have been developed for separations of anions by ion chromatography. A new family of chelating reagents has been synthesized, and selected reagents are being tested for chelating metal ions and determining the various metal ions by chromatographic separation of the chelates. A sample method has been devised for the accurate measurement of column dead time in gas chromatography. [2.4 FTE]

108. *Mass Spectroscopy in Chemical Analysis* R.S. Houk

The general objective is the invention and fundamental study of new techniques for mass spectrometric (MS) analysis. One area of investigation involves the use of the inductively coupled plasma (ICP) as an ion source for elemental and isotopic analysis. This new technique (ICP-MS) was first demonstrated in the Ames Laboratory and has become a major contribution to analytical methodology. This project emphasizes particular aspects of this technique not being studied elsewhere (e.g., improvements in the ion extraction process and MS instrumentation). Use of ICP-MS detection with chromatographic separations for elemental speciation is also being investigated. Based on ICP-MS experience, several novel ways to observe optical spectra from the ICP have been demonstrated. One of these optical techniques provides, for the first time, a reasonable spectroscopic method for determination of halogens in solution (a problem previously addressed only by ion chromatography). Finally, new projects to separate and detect ions via ion trapping and time-of-flight techniques have been initiated. [2.7 FTE]

109. *Chemical Analysis at Liquid-Solid Interfaces* M.D. Porter

This project examines new approaches for the construction and characterization of polymeric and monomolecular films at liquid-solid interfaces. Recent efforts have focused on: (1) probing the structure and reactivity of chemically modified polymer films with *in situ* Fourier transform infrared reflection spectroscopy; (2) examining the relationships between surface roughness and defect structures in monomolecular assemblies; and (3) developing optical sensors with novel chemical analysis capabilities. The methodology based on infrared reflection spectroscopy relates the composition and molecular arrangement (spatial orientation and packing density) of the organic surface structures with their performance as barrier films to solvent penetration and electron transfer. Defect structure efforts

examine the role of the intermolecular interactions between adjacent alkyl chains on the formation of a densely packed monomolecular assembly. The sensor research explores new strategies for developing optical probes for remote-sensing and chemical analysis. [2.1 FTE]

110. Lasers in Analytical Chemistry

E.S. Yeung

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 transient atom sources, such as the laser microprobe, so that quantitation can become more reliable; (2) nonlinear Raman 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 chemiluminescence for trace gas and for surface analysis. [5.6 FTE]

Argonne National Laboratory Argonne, Illinois 60439

Chemistry Division

\$1,199,000

111. Separations Science Related to Nuclear and Hydrometallurgical Technology

E.P. Horwitz

The primary objectives of this project are threefold. First, to design, synthesize, and characterize new classes of aqueous-soluble complexing agents for metal ion separation. These new complexants are designed to be used in conjunction with conventional extractants to achieve unique separations and to avoid waste disposal problems. Second, to design, synthesize, and characterize new classes of metal ion solvent extractants capable of performing very difficult separations from highly acidic media. Third, to investigate third-phase formation in selected neutral organophosphorus-solvent systems, to develop methods of eliminating third-phase formation by modifying the diluent structure and by utilizing specifically designed phase modifiers. All three objectives are directed towards applications in (1) nuclear technology, such as actinide separations, waste processing, and by-product recovery from nuclear waste, and (2) hydrometallurgical processing and groundwater decontaminations. [5.5 FTE]

112. Particle-Induced Desorption/Ionization Mass Spectrometry

J.E. Hunt

The use of energetic particles to impact organic sample surfaces and to induce desorption of secondary ions is a rapidly growing area with practical implications in the field of mass spectrometry. Energetic particles from ^{252}Cf , used to create gas-phase ions in a mass spectrometer, have been directly responsible for the successful mass analysis of thermally labile and nonvolatile

organic compounds. For the first time, small proteins (molecular weights up to 35,000 amu) have become amenable to mass analysis. Well-defined incident particle beams from accelerators have made possible detailed investigations into the mechanisms of desorption. The major concern of this research is a systematic assessment of the desorption yields from solid organic samples as a function of the size, velocity, and chemical nature of the incident particle, with the goal of enhancing and extending analytical mass spectrometry. Unexpectedly strong enhancements in the yield of secondary molecular ions of the analyte can be obtained with fast molecular ions. Multiatomic incident ions may thus be a way to extend the mass range obtainable in mass spectrometry of a host of high-molecular-weight compounds. [2.2 FTE]

Brookhaven National Laboratory Upton, Long Island, New York 11973

Department of Applied Science

\$538,000

113. Analytical Techniques with Synchrotron Radiation and Ion Beams

K.W. Jones, B.M. Gordon

This project investigates new analytical techniques for elemental determinations and chemical speciation using synchrotron radiation from the National Synchrotron Light Source (NSLS). A beam line that will be used as an x-ray microscope/microprobe (XRM) beam line is now being installed. The new beam line is a major step beyond the one used for our initial work on XRM experiments. A monochromator and focusing mirror have been incorporated in the line, and the target position moved closer to the x-ray source point. The x-ray flux at the sample will be increased by approximately three orders of magnitude, and it will be possible to use either white light or monoenergetic photons. It should be possible to use either a collimator or secondary focusing system to make measurements with spatial resolutions below 10 micrometers and detection limits around 1 fg. Related work concerns improvements of detector systems and application of computed tomography and other imaging techniques to enhance the performance of the system. Measurements with ion beams are going on to develop accurate methods for assay of light elements with high sensitivity and excellent spatial resolution. The measurements include application of nuclear reaction methods, proton-induced x-ray emission, and accelerator mass spectrometry. [3.3 FTE]

114. Stationary-Phase Advances for Analytical Chromatography

S.R. Springston

This project focuses on improving separation capabilities in capillary gas chromatography (GC). Separation selectivity will be enhanced by modifying existing stationary phases and creating completely new phases. Concurrently, it will be necessary to reduce the column activity that is typically associated with selective phases and that greatly diminishes column efficiency. These aims are widely recognized by chromatographers striving to enlarge the scope of the technique. Low-temperature plasma discharges, generated *in situ*, offer several means for achieving these goals. Plasmas appear uniquely suited for several different column preparation steps including: cleaning, deactivation, cross-linking of stationary phases, and modifying

stationary-phase polarity. Plasmas are particularly desirable because their energetic nature allows stimulation of various reactions, thus eliminating the need for excessive external heating, which damages the outer polyimide coating of capillaries. Objective measurements of column performance will be taken from the statistical moments of chromatographic peaks. These measurements will support and coordinate the optimization of new fabrication procedures. [1.0 FTE]

Idaho National Engineering Laboratory Idaho Falls, Idaho 83401

EG and G Idaho, Inc. \$199,000

115. Negative Ionization Mass Spectrometry *J.E. Delmore, A.D. Appelhans, D.A. Dahl*

Several gas-phase negative ion formation processes are under study to elucidate the ion formation/decomposition pathways. This past year a study was completed that elucidated the lifetimes of the excited states of the sulfur hexafluoride anion for electron autodetachment as a function of temperature. This system is of great interest for production of high-energy neutral beams for secondary ion mass spectrometry. A system currently being studied produces a variety of negative ions when electrons impact an adsorbate on an electrode. The hydride ion forms in good yield when hydrogen-containing molecules are adsorbed on the electrode. This is another potentially important analytical system, and the fundamental ion formation mechanism needs to be better understood. Other systems are being studied to understand the chemical interactions between ad/absorbates and the substrates as they pertain to gas-phase ion formation. In order to understand these processes, it is necessary to accurately model the motion of the ions in electric and/or magnetic fields. Mathematical algorithms have been developed and converted into computer codes (with graphics) for modeling such systems. These evolving codes have been essential to the success of this project and are also in use by many other scientists at other facilities for related purposes. [1.0 FTE]

Monsanto Research Corporation—Mound Miamisburg, Ohio 45342

Operations Department \$340,000

116. Isotope Separation Research and Development *W.M. Rutherford, B.E. Jepson, R.E. Eppley, W.R. Wilkes*

This project will investigate chemical exchange chromatography and liquid-phase thermal diffusion as techniques for stable isotope separation. The chemical exchange work is directed toward finding metal isotope exchange systems that possess equilibrium single-stage separation factors sufficiently large for practical applicability to metal isotope enrichment processes. The current emphasis is on macrocyclic ligands as metal ion hosts with the ligand immobilized on a solid support to enable the use of chromatographic separation techniques. The liquid thermal diffusion work is directed toward (1) further developing the relationship between the elementary liquid-phase thermal diffusion effect and molecular mass and structure and (2) acquiring an improved understanding of the behavior of the liquid-phase thermal diffusion column and its application to the separation of stable isotopes. [3.2 FTE]

Oak Ridge National Laboratory Oak Ridge, Tennessee 37831

Analytical Chemistry Division \$1,771,000

117. R&D in Secondary Ion Mass Spectrometry *W.H. Christie, D.E. Goeringer, P.J. Todd*

Secondary ionization mass spectrometry (SIMS) and sputter atomization, resonance ionization mass spectrometry (SARIMS) are analytical techniques noted for utility and exceptional sensitivity for analysis of samples containing intractable analytes. Developing an understanding of the fundamental chemistry of these two ionization processes is necessary to optimize their analytical utility. The purpose of this work is to investigate the processes involved in secondary ion emission and atomic neutral sputtering induced by impact of keV primary ions. This is accomplished by studying samples of known chemistry, varying parameters such as ambient pressure of a known gas, primary ion parameters, duration of primary ion bombardment and laser pulse, ion and light optics, sample composition, and so forth. Secondary ionization of organic compounds is studied by using a triple sector MS/MS spectrometer which permits distinction of isomeric ions. Secondary ionization of inorganic compounds and SARIMS are studied using two mass spectrometers which are identical save for the necessary differences in ion source design. Benefits expected from this work are the development of greatly simplified methods that offer improved sensitivity for the analysis of difficult sample types and a better understanding of the mechanisms of secondary ion and neutral emission. [1.9 FTE]

118. Mass Spectrometry R&D for Organic Analyses *G.L. Glish, K.G. Asano, E.H. McBay, S.A. McLuckey*

The focus of this work is to study gas-phase chemistry and physics of ions and to develop and understand techniques to analyze ions in the gas phase. The gas-phase ion chemistry and physics involves the study of unimolecular and bimolecular processes, typically with the technique of mass spectrometry/mass spectrometry (MS/MS). Techniques being developed and investigated for the analysis of gas-phase ions are principally related to mass spectrometry. These include means of ionization, excitation, and analysis, with the main focus on improving the understanding and application of the technique of MS/MS. The benefit of this work will be a better understanding of intrinsic chemical properties, which will lead to better methods of chemical analysis for: (1) mass spectrometry and other charged particle analysis techniques and (2) other techniques that probe fundamental properties of molecules. [2.6 FTE]

119. Advanced Spectroscopic Methods for Chemical Analysis *L.D. Hulet, D.L. Donohue, T.M. Rosseel, J.M. Dale*

This work is currently focused on the development of spectroscopic methods that make use of positrons and heavy ions. The Oak Ridge Electron Linear Accelerator (ORELA) and the Holifield Heavy Ion Research Facility (HHIRF) provide a unique medium for carrying this out. The ORELA is being fitted with a moderator and solenoids for producing a monoenergetic positron beam. A high-resolution, high-efficiency x-ray monochromator is being installed in the EN

Tandem; in the future it will also be fitted to the HHIRF. The construction of both of these new facilities is essentially complete, and they will soon be put into use. In the work of other groups, positron spectroscopy has been mainly applied to the characterization of solids. This will also be done with the ORELA facility, but many new uses will be explored also: (1) the formation of ions for mass spectroscopy, (2) studies of positron capture by ions and Rydberg atoms, and (3) positron-induced radiation damage of DNA. Heavy-ion induced x-ray satellite emission (HIXSE) is being applied to the analysis of alloys and other solids. Chemical shifts in the yield of satellite lines provide information about the electronic structure and bonding. [2.7 FTE]

120. Research Development and Demonstration of Advanced Chemical Measurement Techniques

*J.M. Ramsey, H.H. Ross, R.W. Shaw,
W.B. Whitten, J.P. Young, L.N. Klatt*

This project addresses the use of lasers in advancing spectrochemical analysis techniques. Emphasis is on high-resolution high-sensitivity optical spectroscopy. Doppler-free spectroscopic techniques are being used in low-pressure atom reservoirs to enhance spectral resolution. This combination of spectroscopy and sample preparation significantly reduces inhomogeneous and homogeneous line broadening effects. The advantages of utilizing supersonic expansions in atomic spectrometry are also being explored. New types of spectroscopic sources are being designed for these measurements. Work involves using photorefractive optical elements to control the bandwidth and wavelength of CW dye lasers. Other uses of photorefractive optical elements in laser-based chemical analysis are being explored. The measurement of refractive index based on two-wave mixing in photorefractive materials is currently under study. [3.0 FTE]

121. Mass Spectrometric R&D for Inorganic Analyses

*R.L. Walker, D.L. Donohue, M.P. May,
R.W. Shaw, D.H. Smith, J.P. Young*

The objective of this work is to advance the state of the art in inorganic and actinides 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. Laser-based resonance ionization is studied as a means for vastly improving specificity. Improved methodology for determining various difficult-to-measure elements is investigated. Examples are a high-precision method for determining calcium and the determination of promethium in the presence of excess samarium by resonance ionization mass spectrometry (RIMS). RIMS work provides much fundamental analytical spectroscopy data. For improved sensitivity and more accurate measurements, new work is planned in glow discharge mass spectrometry. [2.3 FTE]

Chemical Technology Division

\$1,384,000

122. Chemical and Physical Principles in Multiphase Separations

*C.H. Byers, O.A. Basaran, T.C. Scott,
J.J. Perona*

This project comprises several fundamental studies that address the use of electromagnetic fields to enhance the efficiency of separation processes. Focus is on improving mass transfer in

liquid-liquid solvent extraction and on analysis of electric field effects in liquid droplet formation and on microscopic droplet transport phenomena. A secondary focus is on exploring the use of magnetic fields in separations processes. Investigations in the area of solvent extraction include mechanics of droplet oscillation and rupture to form interfacial surface area, effects of pulsing electric fields on droplet-continuum hydrodynamics, droplet coalescence, and mass transfer studies. Work is also being continued in the areas of electric field enhanced droplet formation and effects of droplet size on mass transfer driving forces. In addition, studies are being conducted that investigate the effects of high-intensity, high-gradient magnetic fields on the separation of macromolecules. [4.4 FTE]

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

H.D. Cochran, C.H. Byers, C.D. Scott

Fundamental experimental and theoretical studies are focused on relating macroscopic properties of mixtures to intermolecular interactions and molecular correlation functions for the highly asymmetric systems characteristic of extraction by supercritical fluids and adsorption from supercritical fluids. Experimental studies of solubility of transition metal fluorides in supercritical carbon tetrafluoride are under way. Complementary theoretical studies based on distribution function theories from statistical mechanics are continuing; these efforts have already led to new models for solubility and other equilibrium properties. A new technique for measuring adsorption rates from supercritical mixtures based on a surface acoustic wave transducer is being evaluated. Future experiments are under consideration for direct measurement of molecular correlation functions of supercritical mixtures using neutron scattering. [2.1 FTE]

124. Chemistry of Actinides and Fission Products

L.M. Toth, D.J. Pruett, S.A. Sherrow

This project represents perhaps the only continuing fundamental research effort in the area of actinide/fission-product chemistry that is largely concerned with the related behavior in various separations schemes. Because the scope is so broad, the numerous activities encompass many techniques and considerations. Currently, these include: (1) matrix isolation methods to isolate reactive intermediates; (2) neutron/x-ray small angle scattering experiments to define sizes and geometries of colloidal species; (3) photochemical reactions to effect novel separations; (4) vis/ultraviolet spectroscopic studies to define unusual bonding and coordination processes; (5) kinetics/thermodynamic studies of complexes and redox processes; (6) solution/solvation properties of aqueous/nonaqueous systems; (7) ion exchange materials for actinide and lanthanide separations; and (8) macrocyclic ligands. [2.3 FTE]

Chemistry Division

\$871,000

125. Chemical and Structural Principles in Solvent Extraction

*B.A. Moyer, R.A. Sachleben, J.H. Burns,
W.J. McDowell*

The goal of the project is to elucidate the relationship between extractant structure and function in solvent extraction and related separation systems. The approach involves the synthesis of potential extractants and determination of their chemical and

separative properties. Techniques include (1) acquisition and computer-aided analysis of distribution data; (2) structure determination of crystalline model compounds; (3) NMR, UV/vis, FTIR, and Raman spectral measurements; (4) molecular mechanics calculations; and (5) titration calorimetry. Through use of these tools, principles regarding the role of extractant structure emerge and provide the basis for the design of the next generation of extractants. Current project focus is on multidentate and macrocyclic compounds, especially oxa and thia crown ethers, as a means to enhance and control selectivity in the extraction of metal cations from aqueous media. Investigations of synergistic systems containing both macrocycles and cation exchangers continue as the structural requirements (e.g., ring size, substituents, and donor atoms) needed for extraction of alkali, alkaline earth, and first-row transition metals are probed. With the synthesis of a lariat 14-crown-4 ether containing a phosphinic acid side arm, recent efforts have been initiated to investigate the cooperative effect between ionizable functionalities and neutral donors in the same molecule. [5.7 FTE]

**Pacific Northwest Laboratory
Richland, Washington 99352**

Chemical Sciences Department

\$1,216,000

126. Analytical Mass Spectrometry Research

*R.L. Gordon, J.M. Kelley, D.M. Robertson,
J.J. Stoffel(s), J.F. Wacker*

This project advances knowledge and techniques to extend the application of mass spectrometry to problems in chemical and isotopic analyses. Elucidation of pertinent processes at the fundamental level is emphasized. The project (1) determines physicochemical mechanisms responsible for efficient ion production by surface ionization, and (2) obtains methods for the control of surface work function of ion sources. Surface analysis and microchemical separations establish physical properties of surfaces and identify chemical pathways responsible for ion production. Low-power direct-current discharge and laser-assisted negative ionization are being studied as new ionization techniques. [2.8 FTE]

127. Fundamental Phase Partitioning in Supercritical Fluid Chromatography

R.D. Smith, C.R. Yonker

The goal of this project is a fundamental understanding of the kinetic, thermodynamic, and molecular level phenomena related to structure in supercritical fluid solutions relevant to separation and chromatographic processes. In the most general sense, this project is exploring supercritical fluid phenomena in order to bridge the gap between understanding the gas and liquid states. One aspect of this project is focused on gaining an understanding of chromatographic processes for polar and mixed supercritical fluid and solute systems, and the kinetic and thermodynamic limitations upon separations in supercritical media. A second area of concern is the exploration of local molecular structure and organized molecular assemblies (e.g., micelles and microemulsions) in supercritical fluid solutions as a function of fluid density between the gas and liquid limits. Both normal and reverse micelle and microemulsion systems, where the nonpolar phase is a supercritical fluid, are also being investigated as the basis for new separation methods caused by the unusual pres-

sure dependence of phase behavior for these systems. Experimental results are being compared with simple theoretical methods for prediction of fluid-phase structure in the solvation region about a solute molecule. Experimental studies for simple micelle systems where xenon is the continuous fluid phase are being conducted to facilitate understanding of various organized structures in fluids. It is anticipated that this research will form the basis for new separation methods as well as improve understanding of solvation and structure in the liquid phase. [2.2 FTE]

128. Mechanisms of High-Temperature Atomization in Chemical Analysis

D.L. Styris

This project uses mass spectrometry and atomic absorption spectrometry techniques to elucidate mechanisms that control atomization on high-temperature surfaces. These mechanisms are important in establishing the basis needed to broaden and improve applications of those spectrometries that rely on thermal atomization sources. The atoms and molecular species that evolve from these surfaces, during rapid thermal ramping, are monitored in real time. Thermodynamic and kinetic data are then used to help identify and characterize the controlling chemical and physical processes. 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, is also investigated. Mechanisms responsible for chemical matrix effects, such as stabilizing effects of palladium on selenium and on arsenic, are being elucidated. The project is also elucidating atomization interference mechanisms among the Group II A elements. [1.8 FTE]

129. Laser-Based Analytical Techniques

T.J. Whitaker, B.D. Cannon

Laser spectroscopy techniques are being used in this project to learn basic information necessary for the development of new analytical methods and for the improvement of existing methods. The ultimate goal is to improve our capability to measure trace, energy-related materials. Focus is on noble gas isotope analyses. Spectral splittings between metastable-state noble gas isotopes have been measured to determine if it is possible to detect low-abundance isotopes (such as ^{85}Kr , which is a potentially hazardous isotope generated in nuclear facilities, and ^{81}Kr , which can be used for determining the stability of potential waste repository sites) among the high concentrations of naturally occurring stable isotopes. Feasibility was recently demonstrated for a unique noble-gas measurement concept developed under this project in which the desired isotope is selectively deflected by a laser beam and then detected by photon-burst spectroscopy. This demonstration involved what is believed to be the first-ever isotopically selective photodeflection of an atomic beam of metastable atoms. Measurements are also being made to assess a double-resonance ionization mass spectrometry technique that could rapidly measure noble gas isotopes at relative abundances as low as 10^{-12} . These measurements include isotope shifts, hyperfine splittings, transition probabilities, and photoionization cross sections. [1.6 FTE]

Heavy Element Chemistry

Argonne National Laboratory
 Argonne, Illinois 60439

Chemistry Division \$1,510,000

130. Heavy Element Chemistry Research
*W.T. Carnall, J.V. Beitz, L. Soderholm,
 L.R. Morss, J.C. Sullivan*

The project objective is to understand the electronic and bonding properties of the actinide elements, and to use the unique properties of the actinide and the related lanthanides to solve critical fundamental and applied problems. Each activity relates to the nuclear fuel cycle and to other energy and materials research, thus providing basic support for the broad energy development goals of the Department of Energy (DOE). Syntheses of stable and reactive actinide solids are combined with bonding, reactivity, and electronic structure modeling so that actinide solids can be characterized or tailored to optimize desired material properties. Systematic investigations comparing properties among many members of the 4f and 5f series are emphasized. Recent important contributions to the understanding of high- T_c superconducting oxide phases have resulted from the use of this approach. Research in photophysics and photochemistry of the transuranium elements provides new insight into the chemical consequences of excited-state formation and the dynamics of relaxation modes. Use of new sensitive methods of detection support DOE programmatic interests in monitoring waste isolation. Dynamic and thermodynamic parameters that characterize oxidation-reduction and complex formation reactions of actinides in aqueous solutions are probed with state-of-the-art pulse radiolysis and stopped-flow methods. Such investigations enhance the ability to gain a predictive understanding of actinide ion reactions in process chemistry and in the aquatic environment. [9.3 FTE]

Lawrence Berkeley Laboratory
University of California
 Berkeley, California 94720

Materials and Chemical Sciences Division \$1,350,000

131. Actinide Chemistry
N.M. Edelstein

The project objective is to study actinide materials to provide the basic knowledge necessary for their safe and economic use in present and future technology. The project includes preparation of new gaseous, liquid, and solid phases and studies of their physical and chemical properties. Techniques for characterization include x-ray diffraction, optical and vibrational spectroscopy, magnetic resonance, and magnetic susceptibility. Equilibrium and kinetic data for complex formation are measured. From these complementary studies, new insights into the structural and chemical principles of actinide compounds are obtained to design new synthetic schemes to produce new materials. A major aspect is the design and synthesis of sequestering agents for actinide ions. These compounds are intended for use in the treatment of actinide poisoning and for possible application in the treatment of spent reactor fuels. Preparative, structural, and physical studies of new types of organoactinide,

related organolanthanide, and new actinide inorganic complexes are continuing. Studies on optical spectra of free ions and actinide ions in crystals are being pursued in order to understand their electronic structure. [15.0 FTE]

Nuclear Science Division \$100,000

132. Chemistry of the Heaviest Elements
D.C. Hoffman

The objective of this project is to investigate some of the most fundamental chemical properties of elements 102 through 105, which are of particular interest in defining the architecture of the periodic table and in assessing the influence of relativistic effects. The actinide series ends with lawrencium (element 103), and the change in properties in going to elements 104 and 105 is especially important. In addition, relativistic effects have been predicted to become increasingly prominent for the higher Z elements and possible observable effects include anomalous trends in ionic radii and stabilization of different oxidation states relative to lighter homologs. These properties are to be investigated for elements 102 through 105, even with the small numbers of atoms of short-lived nuclides which can be produced. The project includes determining or confirming the most stable oxidation state for each element and the range and stability of other oxidation states accessible in aqueous solutions. Methods will be developed for stabilizing No(III) and deducing its ionic radius. In order to facilitate the studies, a computer-controlled automated chemistry system will be constructed although initial studies will be performed manually. An effort will be made to produce and identify new, longer-lived isotopes of the heaviest elements which will permit more detailed studies of their chemical properties. [1.0 FTE]

Los Alamos National Laboratory
 Los Alamos, New Mexico 87545

Isotope and Nuclear Chemistry Division \$371,000

133. Actinide Chemistry in Near-Neutral Solutions
D.E. Hobart

In the continuing investigation of hard oxygen-donor type ligands for actinide complexation, a Raman spectroscopic study of the entire series of lanthanide oxalate compounds has been completed and work on the actinide oxalates through californium is under way. These ligands are structurally and chemically similar to other strong actinide complexants such as carbonate, phosphate, and humic acids commonly found in the environment. This work is in collaboration with researchers at Oak Ridge National Laboratory. X-ray diffraction and Raman spectral data for berkelium and californium sesquioxalates have been determined for the first time. Solid-state diffuse reflectance and absorption spectroscopies to characterize more fully these complexes are being used. The existence of extended series of stoichiometrically related compounds, such as the lanthanide and actinide oxalates, presents a unique opportunity to study relationships such as ionic radius versus crystal and molecular structure. Work will be extended to other hard oxygen-donor ligands in both solid state and solution. The formation, characterization, and stability of plutonium(IV) colloid by diffuse reflectance spectroscopy and electrochemistry have been investigated. The first high-resolution reflectance spectrum of high-fired plutonium dioxide has been recorded and found to be

nearly identical to the absorption spectrum of the colloidal *sol* of Pu(IV). This result lends support to the earlier suspicion that Pu(IV) colloid is structurally quite similar to plutonium dioxide. Plutonium (IV) colloidal *sol* reacts at a metal electrode surface and can be electrochemically oxidized and reduced under applied potential conditions. Knowledge of the behavior of Pu(IV) colloid is important because of its potential for the transport of radionuclides from a breached nuclear waste repository to the far-field environment. [0.76 FTE]

134. Actinide Organometallic Chemistry A.P. Sattleberger

The project objective is to study fundamental aspects of early actinide (Th → Am) organometallic chemistry. Focus is on: (1) synthesis and characterization of new classes of actinide complexes containing nonclassical ligands, such as alkyls, silyls, amides, phosphides, and thiolates; (2) investigation of actinide-mediated small molecule chemistry, such as the insertion of carbon dioxide and carbon monoxide into actinide-alkyl, -amide, and phosphide bonds; (3) *ab initio* molecular orbital calculations on simple actinide(III) complexes, such as An(NH₂)₃ and An(OR)₃, which are models for known, volatile actinide monomers; (4) synthesis and structural characterization of actinide alkoxide complexes that will serve as useful models for aqueous-phase actinide oxo/hydroxo complexes; and (5) development of low-temperature routes to known and new solid-state actinide materials (e.g., UCd₁₁ and U₆Br₁₂Co) from solution or the vapor phase. Recent results include preparation and structural characterization of the first thermally stable uranium(III) alkoxide complexes, U(O-2,6-R₂C₆H₃)₃ (where R = Me, i-Pr, or t-Bu), and the first uranium(VI) oxo-alkoxide cluster compound, UO₂(O-t-Bu)₂[UO(O-t-Bu)₄]₂. We have also isolated the first homoleptic uranium(III) alkyl complex, U[CH(SiMe₃)₂]₃, prepared a number of simple adducts, LU[CH(SiMe₃)₂]₃ (where L = THF, EtCN, N₂CPh₂), and have begun to investigate the mechanism and thermodynamics of CO₂ insertion into the uranium(III)-alkyl, -amide, and -alkoxide bonds of U[CH(SiMe₃)₂]₃, U[N(SiMe₃)₂]₃, and U(O-2,6-R₂C₆H₃)₃. [0.9 FTE]

Materials Science and Technology Division **\$125,000**

135. Actinide High-Temperature Thermodynamics P.D. Kleinschmidt

The project objective is to measure the thermochemical parameters of actinide compounds and molecules, concentrating on elements other than thorium and uranium. The compounds and molecules studied are the oxides, fluorides, and oxyfluorides, with the neptunium-fluorine and americium-oxygen systems currently being investigated. The enthalpy and entropy of sublimation of the stable solids NpF₃, NpF₄, NpF₅, AmO_{1.5}, and AmO_{2-x} are being measured as well as the bond dissociation energies and standard entropies of the molecules NpF, NpF₂, NpF₃, NpF₄, NpF₅, and NpF₆. These values are systematically compared as a function of atomic number for a given system. From such comparisons and spectroscopic and structural information, the effect of the number of available electrons and number of ligands on molecular stability can be determined. These data are collected using high-temperature Knudsen-effusion mass spectrometry. From trends established for the more readily available actinides, experiments will be designed

to measure the thermodynamic parameters of those actinides that are available in very limited quantities. [0.7 FTE]

Oak Ridge National Laboratory Oak Ridge, Tennessee 37831

Chemistry Division **\$1,361,000**

136. Chemistry of Transuranium Elements and Compounds O.L. Keller, J.K. Gibson, E. Johnson, R.G. Haire, G.F. Payne

The project objective is to understand the progressively changing bonding characteristics of 5f electrons in the actinide series, from one end of the series to the other. A central theme is the role of relativistic effects in causing the actinide series to be unique in its chemical behavior. Accordingly, a theoretical program is incorporated along with the experimental one. Emphasis is on experimental work on the elements (curium through fermium) produced in the National Transplutonium Production Program. In the area of solid-state chemistry, metals, alloys, and compounds are synthesized and then characterized by crystallographic, thermodynamic, optical, and magnetic and specific heat studies. Alloys containing actinides are permitting measurements of fundamental actinide metallic properties, even with very limited amounts of material. For example, the enthalpy of vaporization and accordingly the metallic valence of fermium metal have just been determined using one nanogram of this rare element in each of several supporting lanthanide alloys. A new approach to the search for unusually low oxidation states of the actinides is being conducted at the tracer level in aprotic solvents, using ion exchange as the detector. A program in the area of organometallic chemistry has recently begun. Atomic energy levels calculations have been initiated using atomic relativistic Hartree-Fock programs developed in Europe. A first objective is to determine whether these state-of-the-art programs can give results that are accurate enough to be chemically useful in the actinides. New approaches are also being investigated that will allow the use of powerful parallel processing computer techniques now available. [8.6 FTE]

Chemical Engineering Sciences

Lawrence Berkeley Laboratory University of California Berkeley, California 94720

Applied Science Division **\$327,000**

137. Turbulent Combustion L Talbot, R.K. Cheng

The interaction between turbulence and chemical reactions in premixed and nonpremixed turbulent combustion flows is studied experimentally using laser diagnostic techniques. A theoretical study of premixed turbulent flames using the vortex dynamics method is also being conducted. The objective is to obtain a better fundamental understanding of the turbulent combustion processes in order to develop theoretical models

capable of predicting these processes. Four idealized experimental flow configurations are used: (1) heated wall turbulent boundary layer capable of supporting combustion in fuel-lean mixtures, (2) rod-stabilized turbulent v-flame, (3) Bunsen-type conical turbulent flame, and (4) turbulent flame stabilized in stagnation flow. The nonpremixed turbulent jet flame burner is being designed and constructed. The experiments focus on measuring detailed statistical data of scalars and velocity fluctuations, to study the effects of large heat release on the turbulent flow field. Also deduced are empirical parameters significant to turbulent combustion theories such as the mean reaction rates and the turbulent burning speed. Several quantitative imaging techniques currently being developed will provide further information on the flame structures. Experimental results are compared (1) with the predictions of a deterministic theoretical simulation of premixed turbulent flames (developed in this laboratory) and (2) with predictions of statistical numerical theories developed by others. [3.0 FTE]

Materials and Chemical Sciences Division \$160,000

138. High-Pressure Phase Equilibria in Hydrocarbon-Water (Brine) Systems
J.M. Prausnitz

Phase equilibria are required for efficient design of large-scale separation processes (e.g., distillation and extraction) in the chemical and related industries: processes that make optimum use of raw materials and conserve energy. Since the variety of technologically important fluid mixtures is extremely large, it is not possible to obtain all desired equilibria from experiment. Therefore, the objective of this research is development of molecular thermodynamics for interpretation and correlation of selected phase-equilibrium data toward reliable general prediction of phase equilibria for computer-aided engineering design. The correlations are expressed through semitheoretical physicochemical models. Particular attention is given to systems of primary interest in energy-related industries, especially those concerned with fossil fuels, aqueous mixtures containing electrolytes, fossil fuel-water mixtures, agricultural products, and mixtures encountered in biotechnology. Development of molecular thermodynamics calls for a combination of theoretical, computational, and experimental work, and for simultaneous awareness of progress in molecular science and of realistic requirements for engineering design. [2.2 FTE]

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Theoretical Division \$85,000

139. Thermophysical Properties of Mixtures
J.J. Erpenbeck

The thermophysical properties of mixtures of particles interacting through the hard-sphere potential (and other simple interactions) are evaluated, using the equilibrium techniques of Monte Carlo (MC) and molecular dynamics (MD), as well as nonequilibrium molecular dynamics (NEMD). Properties under investigation include the equation of state and transport properties. The latter include 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" seem

appropriate. Merits of the various numerical techniques in providing thermophysical properties are also considered. In the study of the "synthetic" NEMD technique, extensive MC-MD calculations, using the Green-Kubo method, have been made for the Lennard-Jones fluid near the triple point. The resulting values of the viscosity coefficient are in sharp disagreement with the published NEMD results, being larger by about 40 percent. The source of this disagreement is not yet understood. The transport properties of hard-sphere mixtures have been evaluated for the Enskog theory for the mainstream fluxes and forces of De Groot. Similarly, the mode-coupling theory for the long-time tails for the transport coefficients have been evaluated. Both theoretical results have been compared with the MC-MD results for an isotopic mixture of hard spheres at a volume of three times the close-packed volume. The transport coefficients are found to be in approximate agreement with Enskog (but with significant discrepancies). The long-time tails, however, appear to show rather large differences, with the observed time-correlation functions being rather larger than predicted by the theory, except for the case of mutual diffusion where agreement is observed. [0.5 FTE]

Sandia National Laboratories
Livermore, California 94550

Thermofluids Division-8362 \$349,000

140. Analysis of Reacting, Turbulent Flows
W. Ashurst, A.R. Kerstein, J.-Y. Chen, B. Sanders

This project consists of the development of turbulence prediction methods for application to flows with high Reynolds numbers and large heat release. In each of the methods under study, emphasis is placed on understanding the detailed mechanisms of heat, mass, momentum, and species transport in the mixing region of reacting shear flows. Four distinct modeling approaches are under study, each focusing on a particular aspect of reacting turbulence. The first approach is to continue development of a Reynolds-stress closure model for nonpremixed flows. This time-averaged closure method has been very successful in describing transport phenomena in Sandia National Laboratory's vertical reacting flow facility. The second approach is to continue efforts in vortex dynamics, which has been very effective in describing time-dependent, reacting turbulent flows in complex geometries. The third approach involves a new effort in direct numerical simulation of the Navier-Stokes equations. This work will focus on premixed turbulent flows. The fourth approach is to continue a new statistical pair-exchange procedure where a turbulent flame is propagated by a process of random exchange between pockets of burned and unburned reactants. This method holds great promise as an engineering tool for flame speed predictions. Development and evaluation of the method to assess its accuracy and range of applicability will continue. [2.0 FTE]

Boston University
Boston, Massachusetts 02215

- 145. Study of Intermediates from Transition Metal Excited-State Electron-Transfer Reactions**
M.Z. Hoffman **\$85,000**
Department of Chemistry

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 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 of all the mechanistic steps of the reaction on 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) cage escape yields in the oxidative reduction of $\text{Ru}(\text{bpy})_3^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine) by methylviologen ($\text{N,N}'$ -dimethyl-4,4'-bipyridinium dication; MV^{2+}); (2) the detailed photodynamics of the reductive quenching of $\text{Ru}(\text{bpz})_3^{2+}$ ($\text{bpz} = 2,2'$ -bipyrazine) in the absence and presence of MV^{2+} ; (3) the reductive quenching of $\text{Ru}(\text{bpm})_3^{2+}$ ($\text{bpm} = 2,2'$ -bipyrimidine) and mixed ligand complexes containing bpy , bpz , and bpm ; and (4) the acid-base properties, reactivity, and electrochemistry of the one-electron reduction products of Ru(II) complexes. In addition, an examination has begun of the photophysical properties of new mono- and binuclear Ru(II) complexes containing ligands with extended structures.

- 146. Photoinduced Electron Transfer in Ordered Polymers**
G. Jones **\$95,000**
Department of Chemistry

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 which 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. Two dye/polymer systems have been chosen for investigation: (1) poly-L-tryptophan and its copolymers with poly-L-lysine, combined with the organic dye, eosin, and tertiary amine groups which can be attached, respectively, to N-terminal and C-terminal amino acids of the peptide chain; and (2) polyelectrolytes, including the derivatives of the naturally occurring polysaccharide, carrageenan, which will have cyanine dye counter-ions electrostatically bound to the polymer surface as J-aggregates. Various electron transfer events are proposed including polymer end-to-end charge migration to traps which are synthetically introduced, or electron transfer along a chain of dye counter-ions. Emphasis is 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. Methods employed to study the bound dye systems will include laser flash photolysis, NMR, circular dichroism, and cyclic voltammetry.

Bowling Green State University
Bowling Green, Ohio 43402

- 147. Photoinduced Charge Separation by Polymer-Bound Chromophores**
M.A.J. Rodgers **\$40,000**
Center for Photochemical Sciences

Amphiphilic polymers composed of methacrylic acid, styrene sulfonic acid, or pyrrolidone backbones with covalently linked chromophoric residues at a 1% or less loading are the subject of this work. Work to date has shown that in acidic aqueous media where the polymer chains assume a coiled conformation, significant charge separation occurs when chromophore excited states interact with alkyl pyridinium ions contained in the aqueous phase. Current investigations are aimed at using picosecond laser flash spectrometry methods to characterize the details of the yields of ion pair production at times below a few nanoseconds, on the premise that rapid charge annihilation is probably in competition with charge separation. The outcome of such studies, in terms of ion yields and rapid decay kinetics under different environmental conditions, is expected to aid in understanding the factors governing charge separation and recombination in amphiphilic systems. Another area of interest is in the overall decay of separated ion pairs. Studies will be useful in determining how polymer composition and conformation influence the long-term stability of separated charges.

University of California
Berkeley, California 94720

- 148. Theoretical Studies of Electron Transfer in Complex Media**
D. Chandler **\$98,600**
Department of Chemistry

The structures, distributions, and free energies of the transition states for the prototypical aqueous ferrous-ferric 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 quantal 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.

OFFSITE INSTITUTIONS

Photochemical and Radiation Sciences

University of Alabama
Tuscaloosa, Alabama 35487

141. *Magnetic Resonance and Optical Spectroscopic Studies of Radiation-Produced Radicals*
L.D. Kispert **\$75,000**
Department of Chemistry

The objective of this research is to determine the role of a host lattice in the formation of radicals and excited singlet and triplet states that are relevant to photosynthesis. Emphasis is on determining what is special about carotenoids that natural photosynthetic systems require them as antennae as well as for protection. The host matrix is being manipulated to determine the carotenoid function (protection, quenching, energy transfer, and antenna). Picosecond optical absorption measurements of the lowest excited singlet state of carotenoids yield a lifetime of 10 ps for β -carotene and increase as the chain length shortens. Measurements at low temperature and upon isotopic substitution show that the short lifetimes are a result of a radiationless transition. Triplet-state decay rate constants of tetraphenylporphyrin increase in the presence of carotenoids with carbonyl functional groups. Unfortunately, the carotenoid triplet-state was not observed by EPR in frozen solution, and thus the effect of matrix on carotenoid triplet state lifetime has not been determined. The lifetimes of carotenoid cation radicals are critically dependent on solvent (host matrix), and they can be prepared with the longest lifetime in the solvent CH_2Cl_2 by electrochemical methods. The tendency for carotenoid cation radicals to exhibit exchanged-narrowed EPR lines has prompted the study of intermolecular interactions as a function of host lattice from which exchanged-narrowed EPR lines can be observed. A number of EPR studies have been carried out on conducting polymers, conducting polymer solutions, and conducting crystals.

University of Arizona
Tucson, Arizona 85721

142. *Mechanisms of Photochemical Energy Conversion by Chlorophyll*
G. Tollin **\$100,000**
Department of Biochemistry

The goal of this project is to elucidate the detailed mechanisms involved in light-induced one-electron transfer reactions involving chlorophyll, and electron donors and acceptors (such as quinones, viologens, and redox proteins), occurring in unilamellar lipid bilayer vesicles (liposomes). These studies involve the use of laser flash photolysis to monitor excited-state and radical dynamics and to measure time-resolved absorption spectral changes. Emphasis is on using bilayer structural properties, such as surface charge and inside-outside asymmetry, as a tool for manipulating electron-transfer chemistry and dynamics. The intent is to devise strategies for increasing the yield of the energy-storing products of such reactions, to decrease the

probability of back reactions, and to facilitate secondary electron transfers to external donors and acceptors (i.e., to mimic the solar energy conversion capabilities of natural photosynthesis).

Arizona State University
Tempe, Arizona 85287

143. *Photoinitiated Electron Transfer in Multichromophoric Species: Synthetic Tetrads and Pentads*
J.D. Gust, Jr., T.A. Moore **\$110,000**
Department of Chemistry

The project objective is the synthesis and study of complex molecular devices that mimic natural photosynthetic reaction centers. Results of these investigations will aid in the design of artificial solar energy harvesting systems and increase understanding of natural photosynthesis itself. For example, a molecular tetrad C-P-Q_A-Q_B consisting of a porphyrin (P) linked to a carotenoid polyene (C) and a diquinone moiety (Q_A-Q_B) has recently been prepared. Absorption of light by this species results in the formation of an initial charge-separated state, C-P⁺-Q_A⁻-Q_B, without 50 picoseconds of excitation. A series of electron transfer steps lead from this state to a final charge-separated state, C⁺-P-Q_A-Q_B⁻, which is formed with a quantum yield of 0.5, and has a lifetime of 4 microseconds in some solvents. Electrochemical measurements indicate that the final state preserves about 1 eV of the energy inherent in the absorbed photon. Comparison of the results for this tetrad with those for related model systems indicates that the high quantum yield observed for the tetrad is a consequence of the multistep nature of the electron transfer process. The knowledge gained from the studies of the tetrad is being used to design new tetrad and pentad artificial reaction centers.

144. *Particulate Models of Photosynthesis*
G.R. Seely **\$70,000**
Department of Chemistry

The system under investigation consists of chlorophyll and other amphiphilic substances adsorbed to the surface of particles of polyethylene swollen with tetradecane. The function of the other amphiphile is critical, as it is expected to ligate chlorophyll through the magnesium, to control the association of chlorophyll molecules in part through hydrogen-bonding, and in some cases to charge the particle surface electrically or to accept an electron from chlorophyll excited states. Such amphiphiles confer fluorescence and photochemical properties on chlorophyll and continue to be objects of study. At present, a variety of amphiphiles containing imidazole, a strong ligand for chlorophyll, have been prepared and are under investigation for the photochemical and photophysical properties of chlorophyll bound by them. The reliable estimation of quantum yields and spectra of fluorescence in highly light-scattering systems containing the particles is essential to these investigations. Mathematical and semi-empirical procedures have been developed and tested for correcting observed fluorescence spectra which will improve confidence in future results.

**University of California
Irvine, California 92717**

149. Research in Chemical Kinetics
F.S. Rowland **\$210,000**
Department of Chemistry

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, ^{38}Cl , and ^{18}F atoms are studied with gaseous substrates. Thermalized tritium atoms added to olefinic positions in $\text{Sn}(\text{CH}_2\text{CH}=\text{CH}_2)_4$ and $(\text{CH}_3)_3\text{Sn}(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_3)$ form excited radicals whose pressure-dependent decomposition indicates highly non-RRKM energy distribution because of restricted intramolecular energy flow. Similar studies with thermal ^{18}F and ^{38}Cl are being continued, with tests for the radiation-damage sensitivity of the reaction products. The mechanistic distinction between (1) "anti-Markownikoff" halogen atom addition to vinyl halides and (2) subsequent radical isomerization is under investigation with both $^{35,37}\text{Cl}$ and isotopic substrates, and with ^{38}Cl . Thermal ^{35}Cl attack on C-C bonds is being explored with hydrocarbon and halocarbon substrates. Mechanistic studies of thermal ^{18}F reactions with metallo-organic compounds are being extended to several silicon-based molecules. The reaction rates of bisulfide ion from aqueous hydrolysis of carbonyl sulfide toward metal precipitation, oxidation, and escape of H_2S to the gas phase are being studied in the laboratory, because of their significance toward such competition in oceanic environments. The mechanistic routes for product formation during HO oxidation are being studied with O^{14}CS and $^{14}\text{CS}_2$. Preliminary theoretical calculations are being conducted on the relative stability of various isomeric forms of Cl_2O_2 because of their possible formation in dimerization reactions of gaseous ClO.

**150. Single-Collision Studies of Hot Atom Energy
Transfer and Chemical Reaction**
J.J. Valentini **\$95,000**
Department of Chemistry

This project investigates the dynamics of reactive and energy-transfer collisions of hot atoms and molecules, that is, atoms and molecules having high translational energy. Present studies involve hot hydrogen, deuterium, and oxygen atoms, and hot OH molecules. The collisions of these with HCl, HBr, HI, H_2 , N_2 , CH_4 , CH_3Cl , and other diatomic and polyatomic molecules are being investigated. The hot atoms and molecules are produced by ultraviolet laser photolysis of various stable precursor molecules. Selection of the precursor and variation of the wavelength of the photolysis allow tuning of the translational energy of the hot atom or molecule. The rotational and vibrational quantum state distributions (of the products of the energy transfer and reactive collisions of the hot atoms and molecules) are measured by laser spectroscopy, primarily coherent anti-Stokes Raman scattering (CARS) spectroscopy. These distributions give the state-to-state cross sections and total cross sections for reactive and energy-transfer processes as a function of collision energy. Since these measurements are made under single-collision conditions, the product quantum state distributions and the cross sections provide a direct and sensitive probe of the hot atom collision dynamics. Our experimental studies are complemented by theoretical studies of the collision dynamics of reaction and energy-transfer processes at

high-collision energy. Quasi-classical trajectory calculations are conducted to give quantum-state distributions and cross sections for comparison with the experimental measurements, to provide further insight about the collision dynamics. The objective of this research is to elucidate the dynamics of hot atom and molecule collisions, and to contribute to the development of theoretical models of these processes.

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

**151. Time-Resolved Laser Studies on the Proton Pump
Mechanism of Bacteriorhodopsin**
M.A. El-Sayed **\$125,000**
Department of Chemistry and Biochemistry

In bacteriorhodopsin (bR) systems, the conversion of light energy into chemical energy takes place via conversion first into electric energy. This occurs in two processes: a very rapid and a much slower one in which proton gradients are formed across the membrane. In bacteriorhodopsin, the rapid process occurs via rapid isomerization, which in turn separates the positively charged protonated Schiff base (PSB) from its counter ion. This somehow leads to an increased acidity of the PSB, which then loses its proton to be pumped across the membrane to create the proton gradient in the slow process of light-to-electric energy conversion. This research has concentrated on understanding the mechanism(s) of converting the light energy into electric energy in bR on a molecular level. Much research has been conducted on the behavior of retinal, the chromophore that captures the light energy. This effort will study the protein molecules (e.g., tyrosine and tryptophan) in conjunction with the photocycle that leads to the creation of the proton gradients. It has been shown that isomerization leads to the rapid energy conversion step and that, unlike chlorophyll, bR does not have a macroscopic antenna system to transfer energy, but each absorbing molecule leads directly to isomerization and thus acts as a reaction center. The slow step of energy conversion in bR, the deprotonation process, is being investigated. The effect of changes in pH, temperature, lipid contents, and metal ion content are some of the perturbations presently being used to examine the molecular mechanism of deprotonation. The effect of these perturbations on the protein absorption and luminescence and their time-resolved polarization are also being examined.

**University of California
Santa Barbara, California 93106**

**152. Energy Transformations in Organometallic
Complexes**
R.J. Watts **\$115,000**
Department of Chemistry

This research project is designed to seek and identify orthometalated species which will be useful as photocatalysts in photo-conversion processes. Synthesis and characterization of new species as well as studies of their photophysical and photochemical properties are incorporated in the program. The four areas of major emphasis are: (1) preparation and characterization of reactive orthometalated photoreducing agents; (2) bimetallic and polymetallic orthometalated complexes; (3) bimolecular electron transfer and intramolecular electron transfer in dual

emission systems; and (4) solvent and viscosity effects on energy transfer processes in orthometalated complexes. Projects in area 1 seek to take advantage of the photoreducing power imparted on orthometalated complexes by the sigma-donor abilities of their metal-carbon bonds. Bimetallic complexes that might be useful as both photo-reductants and photo-oxidants as a result of intervalence transfer are being studied in projects in area 2. Area 3 projects emphasize studies of pathways for photoinduced long-range electron transfer in rigid media where either of two excited states might act as either an electron donor or as an electron acceptor. Research in area 4 seeks to clarify the effects of solvent parameters on intramolecular energy transfer in orthometalated complexes which display dual emissions at low temperatures. These studies probe into the fundamental mechanisms for energy transfer and electron transfer in metal complexes and address the special roles of metal-carbon sigma bonds in influencing molecular ground-state and excited-state structures. Correlations between these structural effects and the rates and mechanisms of energy transfer and electron transfer are being sought.

California Institute of Technology Pasadena, California 91125

153. Fundamental Electron Transfer Processes at the Single Crystal Semiconductor/Liquid Interface
N.S. Lewis **\$100,000**
Department of Chemistry **(11 mo.)**

The focus of the research is in three areas: (1) to understand the chemical nature of the semiconductor/liquid interface; (2) to develop working curves for the cyclic voltammetric behavior of semiconductor electrodes; and (3) to understand the short wavelength spectral response of n-Si/liquid junctions. In the first area, the chemical modification of the electrically active trap sites at important semiconductor surfaces has been investigated. Angle-resolved XPS experiments were performed on single crystal (100) n-GaAs surfaces treated with a series of aqueous cobalt metal complexes at pH > 9. The XPS results demonstrated that Co(III) complexes were reduced to the Co(II) state. Cobalt K adsorption edge and EXAFS studies on powers of GaAs exposed to aqueous Co(III) amine complexes at pH > 9 were performed. The edge adsorption position and structure are consistent with an assignment of Co(II). The EXAFS results were extremely similar to EXAFS data taken on bulk Co(OH)₂. The second area of research involves the cyclic voltammetry of semiconductors. Simulations were performed using a model circuit under varying levels of illumination and for different values of the diode barrier height and voltage scan rate. It has been demonstrated that the key parameter is the impedance ratio of the open circuit impedance of the diode to the maximum faradaic impedance in the circuit. A general set of working curves was derived. The third area of research utilized short wavelength photons to study the interfacial kinetics of semiconductors. The interfacial properties of an n-Si/MeOH-LiClO₄-MeFc^{+ / 0} liquid junction are different from that of an n-Si Schottky barrier device. All data agree with the theoretical formulation for interface kinetics proposed by Reichmann and Green.

Clemson University Clemson, South Carolina 29634-1905

154. Intramolecular Energy Transfer Reactions in Polymetallic Complexes
J.D. Petersen **\$125,000**
Department of Chemistry **(19 mo.)**

The coupling of highly absorbing metal centers (antenna fragments) to potentially photochemically reactive metal centers (reactive fragments) is the major focus of this work. Antenna fragments such as polyazine complexes of ruthenium(II) can be covalently coupled to dihydride complexes of rhodium(III) with multidentate bridging ligands and studied photochemically. For example, irradiation of (bpy)₂Ru(BL)Rh(PPh₃)₂H₂³⁺ - where bpy = 2,2'-bipyridine, BL = 2,2'-bipyrimidine (bpm), 2,3-bis(2'-pyridyl)pyrazine (dpp), or 2,3-bis(2'-pyridyl)quinoxaline (dpq) - in the spectral region associated with the Ru(II) → BL metal-to-ligand charge transfer (MLCT) transition results in reductive elimination of H₂. Studies involving mixed-metal complexes bridged by bpm and dpp have been conducted to study the communicative ability of the bridging ligands. For complexes such as (bpy)₂Ru(BL)Fe(CN)₄ and (bpy)₂Ru(BL)Fe(CN)₄⁺, ruthenium based emission is quenched when BL = bpm but not when BL = dpp. These data suggest that electronic participation of the bridging ligand in the MLCT excited state is localized.

University of Colorado Boulder, Colorado 80309

155. Investigation of Redox Processes at Semiconductor Electrode/Liquid Junctions
C.A. Koval **\$140,000**
Department of Chemistry and Biochemistry **(19 mo.)**

Electron transfer processes at InP and WSe₂ semiconductor-solution interfaces are being investigated. Since control of interfacial electron transfer rates is essential for successful operation of electrochemical devices, understanding the kinetics of these reactions has been and remains a challenging and technologically important goal. The WSe₂-acetonitrile system is a nearly ideal polarizable semiconductor solution interface and thereby excellent for fundamental studies. Five n-type and four p-type WSe₂ electrodes were used to obtain kinetic current vs. potential data in solutions containing poised ferrocene redox couples. These experiments revealed that the currents are caused by different mechanisms for different couples and that there is a lack of quantitative agreement between the measured currents and the predictions of theoretical treatments. InP has been investigated extensively with respect to the existence of hot carriers, which could represent an important mechanism for enhanced solar energy conversion. Reduction of organotin halides at p-InP electrodes is being used to establish the existence of hot carriers.

Columbia University
New York, New York 10027

- 156. Laser-Enhanced Chemical Reaction Studies**
G.W. Flynn **\$117,000**
Department of Chemistry

This project employs extremely high resolution infrared diode lasers to study fundamental combustion and collision dynamics and photochemical reaction processes. High-energy atoms are produced by excimer laser photolysis and used as reagents (1) to investigate collisional excitation of individual rotational and vibrational states of molecules and (2) to study the chemical reaction processes occurring as a result of encounters between translationally hot atoms and molecules. Translational energy recoil of the target molecules in collision or chemical reaction processes is probed by measuring the time dependent Doppler profile of the molecular infrared transitions. Quantum state resolved quenching of O¹D atoms, of importance in atmospheric chemistry, is being studied with the same diode laser probe method. These highly energetic and reactive atoms produce vibrational and rotational excitation of molecules by electronic state relaxation of the atom. Formation of O¹D/molecule collision complexes leads either to atom exchange or to simple physical quenching. Reactions of O¹D to produce chemically distinct molecules are also found to occur for some species at a rate which is near the gas kinetic collision frequency.

Dartmouth College
Hanover, New Hampshire 03755

- 157. Photoexcited Charge Pair Escape and Recombination**
C.L. Braun **\$75,700**
Department of Chemistry

The escape and recombination of charge pairs produced by photoexcitation of organic molecules is studied in solids and liquids. Two experimental approaches are used to resolve the picosecond time scale recombination of the geminate charge pairs formed by laser photoionization of solute molecules in liquid hexane. A pump-probe conductivity technique gives useful results but appears to introduce modest measurement bias when compared with decay kinetics recorded by the less-sensitive transient absorption method. 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; no hot electron effects are observed. In solid-state electron donor-acceptor materials, the escape and recombination mechanism is apparently quite different. The time-resolved current that arises from single-photon excitation in the charge-transfer absorption band of the 1:1 mixed crystal, phenanthrene:pyromelliticdianhydride, agrees with a model in which the free charges originate from thermal ionization of singlet-charge transfer excitons which live for many nanoseconds. A number of donor-acceptor geometries are explored in experiments to understand factors that limit efficient charge pair separation.

University of Houston
Houston, Texas 77004

- 158. Charge Separation in Photoredox Reactions**
L. Kevan **\$110,000**
Department of Chemistry

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 and metalloporphyrins in frozen vesicles to produce the cation radical is 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 radical cation with respect to the vesicular structure. The structural effects of modification of the vesicle surface structure and of location control of electron acceptors on the photoionization efficiency are being assessed. Similar studies on the photoionization of N-heterocyclics in micelles are also being carried out. Photoexcited triplet states of chlorophyll in vesicles are being directly detected by light modulated electron spin resonance. Correlations between the triplet state yield and the photoionization yield are being evaluated to delineate the chlorophyll photoionization mechanism in frozen vesicle systems.

Louisiana State University
Baton Rouge, Louisiana 70803-0301

- 159. Theoretical Studies of Electrons and Electron Transfer Processes in Fluids**
N.R. Kestner **\$75,000**
Department of Chemistry

This research project is designed to study excess electrons and electron transfer processes in various fluids, especially those that could be important to energy conversion processes. Current studies are directed to the understanding of electrons in small water and ammonia clusters and how they relate to electrons in liquids. General trends caused by the particular polar molecules are now being obtained. Work is in progress on the role of temperature and pressure. Other studies involve trapping of electrons by hydrated ions like sodium. Elaborate calculations are under way to accurately predict electron transfer rates between hydrated transition ions and to study their interactions with each other. Initial work is on the iron(II)-iron(III) aquo system and the related ruthenium ammonia system. It is found that their hydration shells can easily distort as seen also by neutron diffraction studies. Such calculations require better understanding of the calculation of intermolecular forces in large systems, and thus, some work is under way on the removal of Basis Set Superposition Errors.

Marquette University
Milwaukee, Wisconsin 53233

- 160. Resonance Raman and Photophysical Studies of Polypyridine Complexes of Ruthenium**
J.R. Kincaid **\$75,000**
Department of Chemistry

The detailed characterization of the vibrational spectra of the ground and ³MLCT excited states of the parent complex, Ru(bpy)₃²⁺, has essentially been completed, yielding a physi-

cally realistic force field which reproduces the observed frequencies of five isotopic analogues with acceptable accuracy (1.5% average error). The application of this information to the study of excited-state structure and dynamics is of current interest. In addition, the general transferability of the derived force field will prove useful in our studies of structurally related complexes. Several systems are currently being studied, both in fluid solution and in low-temperature glasses, in order to investigate substituent effects on excited-state structure and dynamics. The ground- and excited-state vibrational spectra are obtained using resonance Raman, time-resolved resonance Raman, and conventional infrared spectroscopies. Studies of these systems in organized assemblies have been initiated. Several such systems are of great interest as a consequence of their potential utility in the design of practical energy conversion devices.

**University of Massachusetts
Boston, Massachusetts 02125**

- 161. *Magnetic Resonance Studies of Photosynthetic Reaction Centers and Porphyrins***
H. van Willigen **\$79,800**
Department of Chemistry

The factors that affect the rate of photoinduced electron transfer from excited-state porphyrin molecules to acceptor molecules are studied with the aid of electron spin resonance (ESR) techniques. Measurements give information on the structure of precursor porphyrin photoexcited triplets, aid the identification of redox ion products, and provide kinetic data. Electron donor molecules being studied are tetraphenyl porphyrin (TPP), various metal substituted TPPs, and water-soluble TPPs. Acceptor molecules of interest include various benzoquinones and potassium ferricyanide. To be able to investigate the kinetics, equipment was built for the performance of time-resolved ESR measurements on transient free radicals with a lifetime as short as 1 microsecond. With this equipment, it is possible to investigate the factors that affect reactions that proceed at close to diffusion-controlled rates.

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

- 162. *Interfacial Systems for Photochemical Energy Conversion***
M.S. Wrighton **\$250,000**
Department of Chemistry

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) surface-confined biocatalysts (to exploit and understand multielectron transfer processes of importance in fuel-forming photoreactions); (3) multicomponent redox molecules (to mimic the essential functions of natural photosynthesis of light absorption, charge-separation, and charge transport); and (4) surface modification reagents (to tailor the properties of electrodes used in photoconversion processes). Unique surface chemistry of semiconductors has led to photoconversion devices with efficiencies in excess of 10% for conversion of sunlight to electricity or fuel (in the form of H₂ from H₂O). Preliminary results show

promising leads in molecular approaches to photoconversion which theoretically will be no less efficient than semiconductor-based devices.

**University of Minnesota
Minneapolis, Minnesota 55455**

- 163. *The Contribution of Electronically Excited States to the Radiation Chemistry of Organic Systems***
S. Lipsky **\$97,000**
Department of Chemistry

Photophysical properties of organic molecules are being studied that have relevance in determining their behavior when subjected to high-energy radiation. Because the formation of ion pairs appears to be an important precursor of chemical damage in irradiated liquids, recent studies have concentrated on ion-pair properties. These are generated by photoionization, and their decay is observed by (1) recombination (to give fluorescence) and (2) "escape" (to give photocurrent). These observations are made as functions of photon energy, nature of the liquid, concentration of electron scavenging impurities, and strength of externally applied electric and magnetic fields. Current work includes (1) measurement of the effect of low concentrations of highly electron-affinic scavengers to enhance ion-pair escape probabilities, (2) measurement of the photoionization yield and electron thermalization range spectra of aromatic solutes in nonpolar liquids, and (3) measurement of the transient displacement currents and transient fluorescence intensities induced by pulsed vacuum ultraviolet excitation of saturated hydrocarbon solutions. The magnetic field alters the yield of fluorescence by influencing the probability that recombining pairs are triplet or singlet. The magnitude of this effect provides information on loss-of-spin coherence because of electron attachment and spin thermalization processes.

**National Bureau of Standards
Gaithersburg, Maryland 20899**

- 164. *Pulse Radiolytic Studies of Inter- and Intramolecular Electron Transfer Processes***
P. Neta **\$195,000**
Center for Chemical Physics

Electron transfer processes are studied by the pulse radiolysis technique. Reactive intermediates are produced by irradiating a solution with an electron pulse, and the kinetics of their reactions are followed by time resolved absorption spectrophotometry. The current studies are concerned with kinetics, thermodynamics, and mechanisms of reactions of organic and inorganic radicals and unstable oxidation states, in aqueous and nonaqueous solutions. Focus is on the study of electron transfer reactions of metalloporphyrins that may be applicable to solar energy conversion systems. These include one-electron reduction and oxidation to radical anions and cations or to unstable oxidation states and the subsequent reactions of the resultant species. Important reactions of these species are those involving colloidal catalysts that may lead to decomposition of water to hydrogen and oxygen. Current studies are concerned with the mechanism of reaction between metalloporphyrin radical cations and metal oxide colloids, and the effect of electrostatic charge on these processes, which lead to oxygen evolution under

certain conditions. Similarly, metal colloids are studied for the process of hydrogen evolution from water, utilizing either a porphyrin radical anion or radicals derived from other molecules as the reductants. Studies are also conducted on organic peroxy radicals and inorganic radicals to understand the mechanisms of their reactions and to determine the basic properties of these important species.

University of Nebraska
Lincoln, Nebraska 68588-0304

165. Electrochemical and Optical Studies of Model Photosynthetic Systems
T.M. Cotton **\$87,800**
Department of Chemistry

A functional model of the bacterial photosynthetic reaction center based upon Langmuir-Blodgett multilayer constructions implies control of distances, spacing, and orientation of the individual components. Traditional methods of forming multilayer systems that contain chlorophylls are not always adequate for controlling the orientation of these pigments; therefore, new techniques are under development. A method of great promise entails the formation of contour-specific template sites in monolayers of polymerized silanes that specifically recognize the contour of the chlorophyll macrocycle, rejecting closely similar molecular shapes. By this means, it is possible to construct cavities on a monolayer surface that contain pairs of chlorophyll sites of known spacing and orientation. The adsorption of monomeric chlorophyll into these sites produces pairs of chlorophylls that are not covalently bonded. This is evidently the first instance of a unique construction that does not depend on covalently bonded chlorophyll dimers. This system is being studied as a model of the photosynthetic special pair found in the reaction center. Characterization has been by means of surface enhanced resonance Raman spectroscopy (extremely sensitive and species-specific), electrochemistry, optical adsorption, and fluorescence spectroscopies. These monolayer templates can also be used as the first layer in multilayer arrays formed by Langmuir-Blodgett transfer.

166. High-Energy Halogen Atom Reactions Activated by Nuclear Transformations
E.P. Rack **\$75,000**
Department of Chemistry

The major objective of this project is to understand the stereochemistry, energetics, and systematics of highly energetic halogen atom homolytic bimolecular substitution reactions (S_HH^2) at the chiral centers of enantiomeric and diastereomeric molecules in the gas and condensed phases. In an attempt to ascertain kinetic energy effects, the stereochemistry of exothermic thermalized fluorine and chlorine atom homolytic bimolecular substitution at chiral centers is studied. Specifically conventional nuclear methods are used to obtain information in the following areas: (1) energetic F, Cl, Br, and I stereochemistry and mechanisms with chiral 2-halopropionyl halides and related substrate molecules; (2) stereochemistry of energetic halogen-for-halogen substitution reactions with *d,l*, *meso*-2,3-dihalobutanes; (3) stereochemistry of thermalized F and Cl exothermic substitution reactions with chiral 2-halopropionyl halides and *d,l*, *meso*-2,3-dihalobutanes; and (4) calculations of conformational energies for 2-halopropionyl halides and 2,3-dihalobutanes (using molecular-mechanics techniques).

Reactions of ^{82}Br and ^{130}I , activated by isomeric transition, are studied in liquid aqueous solutions of alkyl halides and halogenated biomolecules to determine the applicability of various models such as the Auger effect coulombic explosion model to liquid state systems. Practical applications of recoil atom chemistry to activation analysis of biological or environmental samples are conducted.

University of North Carolina
Chapel Hill, North Carolina 27514

167. Energy Conversion Processes Based on Molecular Excited States
T.J. Meyer **\$115,000**
Department of Chemistry

The underlying theme of the work is the development and exploitation of transition metal complex based excited states for energy conversion applications. A combination of synthetic and photophysical experiments are being utilized to explore excited state properties and how those properties can be varied systematically by controlled synthetic changes. The second major theme of the work is the incorporation of these metal complexes into complex molecular assemblies as a basis for energy conversion applications. Transition metal complexes are being incorporated into polymeric films on a variety of substrates with the goal of creating controlled microstructures for energy conversion applications.

University of North Carolina at Charlotte
Charlotte, North Carolina 28223

168. Oligomer and Mixed-Metal Compounds, Potential Multielectron Transfer Agents
D.P. Rillema **\$83,800**
Department of Chemistry

The photophysics of bimetallic rhenium(II)/rhenium(I) and ruthenium(II)/rhenium(I) complexes with attached electron donor and electron acceptor ligands is currently being explored. New ligand systems have been synthesized. The ligand HAT is a bipyridine analogue with three bidentate sites capable of binding up to three different metal centers. The ligand *py-pm* and the $[\text{Ru}(\text{bpy})_2(\text{py-pm})]^{2+}$ complex were synthesized, and the ultimate goal of forming the orthometalated, mixed-metal platinum complex, $[\text{Ru}(\text{bpy})_2(\text{py-pm})\text{PtCl}_2]^{2+}$, is being explored. New metal systems have also been investigated. Both cobalt and chromium complexes of heterocyclic ligands have been synthesized. The preparation of cobalt complexes appears straight forward; chromium heterocyclic ligand complexes, however, will require the design of new strategies and the development of new synthetic skills in order to be successful. A new platinum(II)/ruthenium(II) complex has been obtained that contains two platinum centers and one ruthenium center. The complex is paramagnetic. A-frame rhodium binuclear complexes are also being investigated. These complexes luminesce weakly and have short-lived excited states.

Northwestern University
Evanston, Illinois 60202

169. *Intramolecular Electron-Transfer Rates*
J.T. Hupp **\$85,000**
Department of Chemistry

This project involves: (1) construction of pulsed-accelerated flow and pulsed-laser instruments for fast electron-transfer rate measurements; (2) invention and synthesis of multiple-site target molecules for intramolecular rate studies; (3) application of time-dependent Raman scattering theory to the question of inner-shell reorganization in charge-transfer reactions; and (4) further development of electrochemical methods for gauging electronic coupling. From preresonance Raman experiments, a complete mode-by-mode dissection of the vibrational reorganization process in a prototype reaction has been achieved: metal-to-ligand charge transfer in $(\text{NH}_3)_4\text{Ru}(\text{bpy})^{2+}$ (bpy = 2,2' bipyridine). Fourteen separate modes contribute measurably (>0.5%) to the reorganization energy. The contributions from the metal-ammonia modes are found to be significantly tunable by ligand-solvent hydrogen-bonding interactions. A related study has been carried out for two metal-to-metal (or intervalence) charge-transfer chromophores: $(\text{NC})_5\text{Fe}^{\text{II}}(\text{CN})\text{Ru}^{\text{III}}(\text{NH}_3)_5^-$ and $(\text{NC})_5\text{Fe}^{\text{II}}(\text{CN})\text{Os}^{\text{III}}(\text{NH}_3)_5^-$. For the former, Raman scattering can be observed from both redox sites; for the latter it was found that enhanced scattering, and therefore vibrational trapping, occurs only at the hexacyano site.

Oregon Graduate Center
Beaverton, Oregon 97006

170. *Fundamental Studies in Oxidation-Reduction in Relation to Water Photolysis*
J.K. Hurst **\$114,700**
Department of Chemical and Biological Sciences

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. Emphasis has been placed in recent studies on objectives (2) and (3). It has been demonstrated that methyl viologen (MV^{2+}) bound to anionic dihexadecylphosphate vesicles is capable of mediating transmembrane oxidation-reduction by a mechanism that involves transverse diffusion of MV^+ radical cations. This constitutes a breakthrough which is crucial to developing a detailed understanding of reaction mechanisms in microphase-organized redox systems. Ongoing research indicates that radical anions from monoalkylviologens possessing long alkyl chains are markedly less mobile, and therefore mediated transmembrane redox must occur primarily by electron tunneling mechanisms in these systems. This behavior has been rationalized in terms of a structural model in which the long chain analogs, but not MV^{2+} , intercalate within the bilayer, effectively halving its width. Ongoing collaborative efforts are directed at obtaining structural information to evaluate the model and developing theoretical models for the transmembrane redox dynamics based on statistical methods. Also under investigation are a series of

dimeric ruthenium μ -oxo ions as potential water-oxidation catalysts. Contrary to earlier literature reports, it is found that $[\text{Ru}(\text{EDTA})]_2\text{O}$ ions have no catalytic activity. The earlier studies were based on measurements with a Clark polarographic electrode and may have confused CO_2 formation for O_2 . These studies employ mass spectrometric analyses.

Pennsylvania State University
University Park, Pennsylvania 16802

171. *The Gaseous Free-Radical and Ion Chemistry of Silanes, Germanes, and Phosphines*
F.W. Lampe **\$82,000**
Department of Chemistry

This research project includes five 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 organic substrates. The second activity involves (1) elucidation of the ion-molecule reactions characteristic of ionized silane, germane, and phosphine, and silane-germane, silane-phosphine, and germane-phosphine 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. The last activity involves developing new aspects of free-radical synthesis of inorganic compounds of silicon, germanium, and phosphorus.

Princeton University
Princeton, New Jersey 08544

172. *Surface Chemistry at Semiconductor-Electrolyte Interfaces*
A.B. Bocarsly **\$115,000**
Department of Chemistry **(15 mo.)**

This study encompasses the role of surface chemistry in photodecomposition processes occurring at the cadmium chalcogenide-electrolyte interface as well as primary processes associated with water oxidation at stable n-type semiconductors. Recent work has focused on the surface chemistry of n-CdX (X = S, Se, Te) photoelectrodes in a $\text{Fe}(\text{CN})_6^{4-/3-}$ electrolyte. Illumination of such interfaces produces a layer of cadmium ferrocyanide on the electrode surface. This overlayer has alkali cation exchange properties. Iron sites in this layer are electroactive and support mediated charge transfer from the semiconductor to solution electroactive species. To date, both $\text{Fe}(\text{CN})_6^{4-}$ and ascorbate have been investigated as the solution species. 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. A model with good predictive capabilities has been established for this system. This model has led to the development of n-CdSe based cells with good stability and monochromatic light energy to electricity conversion efficiencies (488 nm) of 30 to 40%. In a separate investigation of n-TiO₂ photoelectrolysis (water) cells using laser-induced optical transients, it has been found that the mechanism of water oxidation varies with the pH of the electrolyte. In acid, an outer sphere channel is followed, while in base the predominate reaction channel is inner sphere. This latter process is very efficient and involves the formation of a "Ti-OH" surface site. Any process that decreases the number of surface titanium sites serves to decrease the photoelectrochemical efficiency of such cells.

173. Photochemistry of Metalloporphyrins
T.G. Spiro **\$182,000**
Department of Chemistry

The photochemistry of metalloporphyrins is being explored with a view toward developing new photoenergy transfer catalysts. Porphyrin cation radicals, the primary product of electron transfer reactions, have been studied by resonance Raman spectroscopy. The spectra are being assigned and analyzed, and new features are emerging which provide useful information about the structural distortions on radical formation. Time-resolved Raman techniques are under development in order to monitor the spectra of porphyrin excited states. These will be applied to linked porphyrins which show optical evidence for electron transfer photochemistry. 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, will be developed.

University of Rochester
Rochester, New York 14627

174. Femtosecond Studies of Electron Transfer Processes at Semiconductor Interfaces
R.J.D. Miller **\$85,000**
Department of Chemistry

Interfacial electron transfer is one of the most fundamental steps in surface reaction processes and is the key step in many solar energy transduction schemes. Three new, surface-specific, optical spectroscopies have been developed for the direct study of the electron transfer event. Holographic gratings, written in the form of free electron hole carriers, have demonstrated that electron transfer at the n-TiO₂ (001)/H₂O interface involves thermalized hole carriers at the atomic surface. The hole carrier mass ($m_h^* \geq 3$), thermalization dynamics, and interfacial electron transfer rate constants have been determined and are all consistent with a thermalized electron-transfer mechanism involving adsorbed hydroxide as the electron donor. Optical excitation of surface acoustic waves, using grating excitation, has given direct evidence for a phase change of the water layer to a solid phase at the TiO₂ surface boundary. This new optical method is extremely sensitive. Light diffraction detection in the presence of an electron-hole pair phase grating for reference heterodyne detection enables a detection limit for surface displacements of 10⁻³ Å. Studies of n-GaAs (100) have also been conducted. In this high mobility material, surface state trapping

is found to occur in less than 30 psec. The nonlinear optical properties of the initial trap indicate a highly delocalized site, i.e., a structural defect and not a molecular impurity. The other new optical method relies on the electro-optic effect to measure changes in electron density at the surface. A crystal distortion that occurs upon changes in trap occupation number makes this technique extremely sensitive to surface state dynamics. Both grating and electro-optic surface state studies indicate that shallow defect states are the initial intermediate in the overall interfacial electron-transfer mechanism at the GaAs (100) surface.

175. Applications of Photoinduced Electron Transfer and Hydrogen Abstraction Processes to Chemical and Electrochemical Conversion Processes
D.G. Whitten **\$115,000**
Department of Chemistry

These investigations center largely on light-induced electron transfer reactions in solution and at interfaces, and the formation of and reactivity in inclusion complexes in which hydrophobic or surfactant substrates are "guests" with amylose or carboxymethylamylose as the host. Electron transfer reactions focus mainly on processes in which visible light can be employed to break strong covalent (e.g., C-C) bonds in organic molecules, such as diamines, amino alcohols, and amino acid derivatives. The studies on host-guest inclusion complexes are directed at demonstrations of novel photochemical reactivity of entrapped guests, which can be related to the specific microenvironment provided by the complex.

University of South Florida
Tampa, Florida 33620

176. Frontier Orbital Symmetry Control of Intermolecular Electron Transfer
B. Stevens **\$110,000**
Department of Chemistry **(18 mo.)**

The correlation of electron-donor-acceptor (EDA) frontier π -orbitals belonging to the same symmetry species of the 1:1 donor-acceptor complex point group, provides a basis for the classification of these complexes as exciplexes or as EDA complexes and identifies their intermediary role in adiabatic or diabatic intermolecular electron-transfer processes. Specifically, exergonic geminate recombination of radical-ion pairs, formed by photoinduced charge separation, is predicted to be adiabatic (and fast) for strong EDA complexes, but diabatic (and slow) if the intermediate behaves as a weak exciplex. Rates of photoinduced electron transfer and of geminate charge neutralization are being determined for donor-acceptor systems identified as potential intermediates in adiabatic or diabatic electron-transfer processes, in order to confirm the selection rules predicated on orbital correlation. Donor-acceptor systems include the triad DDA where the donor dimer assumes either a cofacial or a coplanar configuration, and extended systems exemplified by terminally functionalized polyaryls that are expected to form twisted internal charge transfer states.

Stanford University
Stanford, California 94305

- 177. Energy Transfer Processes in Solar Energy Conversion**
M.D. Fayer **\$122,000**
Department of Chemistry

Picosecond optical nonlinear experiments and particular ultrafast holographic grating experiments are being used to study the time dependent dynamics of the electron transfer process. Electron transfer is often followed by back transfer of the electron. This quenches the active molecules before chemistry has taken place. The first detailed experimental study has been completed of the ultrafast dynamics of such processes in solid solutions. Exact statistical mechanical treatment of the kinetics of the processes has been developed. Advances have also been made in understanding electronic excitation transport in complex systems. The first direct indications have been found that transport at room temperature in solid polymeric solutions is dispersive (i.e., it occurs among an inhomogeneous energy distribution of molecules). This will modify existing concepts of excitation transport in room temperature systems. A theory has been developed to describe dispersive excitation transport in complex (nonrandom) systems.

Syracuse University
Syracuse, New York 13244-1200

- 178. Photochemical Solar Energy Conversion Utilizing Semiconductors Localized in Membrane Mimetic Systems**
J.H. Fendler **\$95,500**
Department of Chemistry

Conversion of solar energy to chemical energy continues to be the main objective of this project. Components of the photosynthetic apparatus are being reconstructed in organized surfactant assemblies. Emphasis is on the development of separate sacrificial reduction and oxidation systems which result in the photodecomposition of water to hydrogen and oxygen, respectively. Colloidal semiconductor particles in surfactant vesicles and bilayer lipid membranes are used as sensitizers and catalysts, while advantage is taken of viologens as relays.

University of Tennessee
Knoxville, Tennessee 37996

- 179. Studies of Radiation-Produced Radicals and Radical Ions**
T.F. Williams **\$105,000**
Department of Chemistry

The general objective is to characterize the structure and reactivity of organic free-radical and radical ion intermediates generated by irradiation of molecular systems. Radical cations are generated radiolytically in Freon matrices at low temperatures, while radical anions are similarly produced and stabilized in hydrocarbon matrices, the pertinent reactions involving positive-hole transfer and electron capture, respectively. Radical ions can also be generated photochemically by electron transfer to excited states of strong electron acceptors or by redox reactions on surfaces of semiconductor colloid particles such as titanium dioxide. Electron spin resonance (ESR) and optical spec-

troscopy are used to characterize these paramagnetic species; measurements of g factors and hyperfine coupling constants are being made on isotopically labeled radicals to obtain information about molecular geometry and spin density distribution. Specific projects include studies of (1) radical cation structure and solvent interactions; (2) unimolecular rearrangements (ring opening, hydrogen transfer, cyclization) and ion-molecule reactions of radical cations; (3) fluorocarbon and Freon negative ions, including dissociative processes leading to neutral radical formation; and (4) the photogeneration of radical ions in solution and at colloidal semiconductor surfaces.

University of Texas
Austin, Texas 78712

- 180. Organic Redox Phototransformations at Chemically Modified Surfaces**
M.A. Fox **\$110,000**
Department of Chemistry

This research project seeks to establish the mechanisms of organic redox reactions that occur upon photoexcitation of native and chemically modified semiconductor surfaces. New catalysts are being designed to act as relays for multiple electron transfer. Organometallic coordination polymers and N-alkylated nicotinamide derivatives are being tested as vehicles for catalytic reduction of solution phase substrates. New electrode materials prepared for electrocatalytic studies are being evaluated for high turnover catalytic sequences. Techniques for anchoring the specifically designed electrocatalysts include covalent binding, electrosorption, and chemisorption of redox active polymer layers. Polymers with pendent chromophores are being synthesized in order to produce materials capable of efficient light collection and vectorial energy migration.

- 181. Studies of Photochemically and Electrochemically Driven Electron Transport in Zeolites**
T.E. Mallouk **\$77,400**
Department of Chemistry

This project involves the study of self-organizing molecular electron transport chains in zeolites and related aluminosilicate host solids. Spatial ordering of molecular assemblies containing two, three, or four photoactive/electroactive components is achieved via ion-exchange and size-exclusion effects. The vectorial nature of electron transfer in these systems is studied electrochemically and by flash photolysis/transient absorbance technique. Covalently linked sensitizer-acceptor molecules adsorb on the outer surface of zeolite L and transfer electrons to secondary acceptors within the bulk. An important goal of this project is to maximize the quantum efficiency for photochemical charge separation in these multicomponent systems. Chemically modified zeolites that contain noble metals and oxide semiconductors within their framework have been prepared and characterized. With appropriate sensitizers bound to the surface of these materials, it should be possible to evolve hydrogen from water photochemically, using nonsacrificial electron donors. Electron transfer quenching of surface-bound ruthenium polypyridyl complexes by zeolite-encapsulated semiconductors and by anionic solution-phase electron donors is being studied.

182. Photoinduced Charge Separation by Polymer-Bound Chromophores
S.E. Webber **\$40,000**
Department of Chemistry

Aromatic molecules have been covalently bound to water soluble polymers, especially polyacids. It has been found that under conditions when the polyacid is in a collapsed conformation (pH < 5), singlet state quenching of the aromatics with various substituted viologens often leads to ion pair separation with a quantum efficiency on the order of 0.5. This process does not occur at higher pH's where the polyacid is in an extended conformation. This process is not particular dependent on the aromatic chromophore, having been observed for various substituted anthracenes and perylene (but not pyrene). We have also prepared water soluble polymers with alternating phenanthrene-methacrylic acid moieties. These polymers exhibit efficient down-chain energy transfer to a minority trap species (e.g., 1 mol % of anthracene). This permits extension of the spectral range of these polymeric photoreagents beyond that of the minority photoreaction center.

Washington State University
Pullman, Washington 99164-4630

183. Investigations of Charge-Separation Processes in Metal Complexes
G.A. Crosby **\$85,000**
Department of Chemistry

The project objective is to investigate new types of metal complexes that show promise as photosensitizers for solar energy conversion. Coordination complexes of Zn(II), Cd(II), and Cu(I) are studied by luminescence and thermal modulation spectroscopy both in crystalline solids and in low-temperature glasses. Complexes are being designed and synthesized with near-degenerate excited electronic configurations of radically different charge distributions. The objective is to define the molecular determinants of barriers between charge localized and charge separated states such that the population of the latter can be controlled. Measurements of decay times and spectra as a function of temperature (4 to 120 K) have been initiated to determine barrier parameters. X-ray determinations are also under way to relate structure to the barrier dimensions. The method of thermal modulation spectroscopy is being refined in order to be used on these substances in glasses and in solids. The studies are being extended to Pt(II) species that also exhibit LLCT excited configurations at low energies.

Washington University
St. Louis, Missouri 63130

184. Reaction Studies of Hot Silicon, Germanium, and Carbon Atoms
P.P. Gaspar **\$95,000**
Department of Chemistry

The project goal is to determine: (1) the reactions of high-energy silicon, germanium, and carbon atoms; (2) how their reactions take place; and (3) how the reaction pathways are influenced by the energy and the electronic states of the free atoms and of the reactive intermediates that they produce. Silicon, germanium, and carbon atoms are formed with high kinetic energies and electronic excitation by nuclear transfor-

mations such as $^{31}\text{P}(n,p)^{31}\text{Si}$, $^{76}\text{Ge}(n,2n)^{75}\text{Ge}$, and $^{12}\text{C}(p,pn)^{11}\text{C}$, and at thermal energies by evaporation of the pure elements. A nearly complete picture of the primary reactions of silicon atoms recoiling in phosphine-silane mixtures has been developed, with the finding that silyl and disilanyl radicals, $^{31}\text{SiH}_3$ and $^{31}\text{SiSiH}_5$, are formed as minor, but mechanistically revealing, reactive intermediates. The role of recoiling silicon ions $^{31}\text{Si}^+$ has been quantitatively assessed via the yields of alkyl group abstraction products.

Wayne State University
Detroit, Michigan 48202

185. Photoinduced Charge and Energy Transfer Processes in Molecular Aggregates
J.F. Endicott **\$125,000**
Department of Chemistry

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 the 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 transients using very sensitive detection techniques. In some instances the behavior investigated may have general significance, as in studies of the electronic factors governing charge or energy transfer processes in bimolecular and unimolecular systems. In other instances the photoinduced behavior is more targeted in order to resolve specific problems characteristic of limited classes of molecules. The implications of the models that develop are explored in a variety of systems. Thus, for example, the inference that charge-transfer perturbations can facilitate donor-acceptor coupling in energy-transfer systems has led to the discovery of electron-transfer systems in which charge transfer perturbations play a similar role. The further development of these ideas will be used in designing new systems in which such effects may be manifested in spectroscopic behavior.

186. Dynamics of Charge-Transfer Excited States Relevant to Photochemical Energy Conversion
E.C. Lim **\$90,000**
Department of Chemistry

This project involves fundamental studies of the factors that influence the rate of electron transfer. Current emphasis is on the study of charge neutralization and charge separation in diarylalkanes and $b\pi$ - $a\pi$ charge-transfer complexes. A novel biphotonic laser excitation scheme is used to create intramolecular ion pairs in diarylmethanes via bicimers (dimeric species formed by the association of two identical, electronically excited molecules). The temporal characteristics of the ion pairs are then probed by laser kinetic spectroscopy to identify the mode and rate of their decays. The photophysical properties of electron donor-acceptor complexes in supersonic free jet are compared with those in condensed phase to obtain information concerning solvent and temperature dependence of nonradiative decay processes of charge-transfer excited states, including charge neutralization. The effects of vibrational and rotational degrees of freedom on the decay rates and conformational isomerization are also examined from the comparison.

Chemical Physics

Aerospace Corporation
Los Angeles, California 90009

- 187. *A Shock Tube Study of the Reactions of Hydroxyl Radicals with Combustion Species***
J. Bott, N. Cohen **\$75,000**
Aerophysics Laboratory

The project objective is to use shock tube techniques to measure the rate coefficients for OH reactions important for understanding and predicting hydrocarbon combustion. The experiments are performed at combustion temperatures of 1,200 K and higher and at near-atmospheric pressure. The first series of experiments was devoted to selected reagents for which only one reaction was possible, namely H₂, CH₄, and *c*-C₅H₁₀. The rate coefficients for reactions of OH with these three species were measured and found to be 2.7×10^9 , 2.6×10^9 , and 2.8×10^{10} L/mol-s, respectively, all at 1,200 K. Measurements have also been made for *i*-C₄H₁₀, CH₃OH, CH₃COCH₃, and C₂H₄; the data are being analyzed. Other reagents to be studied include propylene, acetylene, formaldehyde, acetaldehyde, ethanol, and iso-octane. Transition state theory calculations will be used to relate the measurements to other data at lower temperatures so that reliable temperature dependences of the rate coefficients under study (and those of analogous reactions) can be established.

University of Arizona
Tucson, Arizona 85721

- 188. *Chemical Activation of Molecules by Metals: Experimental Studies of Electron Distributions and Bonding***
D.L. Lichtenberger **\$90,000**
Department of Chemistry

Photoelectron spectroscopy is used to provide detailed and independent information regarding the electronic interactions of organic molecules with transition metals. The experimental program is designed to establish a more formal relationship between measured molecular ionization energies and thermodynamic bond dissociation energies in organometallic molecules. This relationship builds on the contribution of ionization energies of simple thermodynamic energy cycles. The value of this relationship has been demonstrated in a continuing study of the electronic factors that contribute to carbon-hydrogen bond activation by metals. For example, a photoelectron study of the relative bond strengths of early transition metal M-C and M-H bonds in substituted niobocenes and tantalocenes has led to a more complete understanding of the electronic energy factors of olefin insertion into a metal-hydride bond. Important information has also been obtained on metal-methylene, metal-alkylidyne, and metal-heteroatom multiple bonding interactions and their influence on the chemistry of these species.

Arizona State University
Tempe, Arizona 85287

- 189. *Electronic Structure and Reactivities of Clusters Containing Heavy Atoms***
K. Balasubramanian **\$78,540**
Department of Chemistry

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 could provide important clues to our understanding of catalysis and chemisorption. Electronic properties, such as ionization potentials, electron affinities, and so forth, 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 Ga₃, In₃, Ag₃, Au₃, and Pd₃ 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 Pd₂, Rh₂, Zr₂, 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 M + H₂ and M₂ + H₂. The potential energy surfaces of AgH₂, AuH₂, RhH₂, ZrH₂, YH₂, and so forth, are being determined with the objective of understanding the reactivities of these atoms with H₂. The Pt₂ + H₂ system is 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.

Brown University
Providence, Rhode Island 02912

- 190. *Interactions of Molecules with Surfaces***
E.F. Greene **\$80,000**
Department of Chemistry

Alkali atoms ionize at equilibrium when they are close enough to surfaces of metals or semiconductors. The ion energy is reduced by its attraction for the surface represented as an image charge inside the bulk. Beams of sodium, potassium, and cesium atoms directed at silicon, tungsten, or platinum surfaces at kinetic energies below about 0.6 eV become trapped by an electrostatic barrier and thus equilibrate with the surface, subsequently desorbing at a rate controlled by the surface temperature. At higher energies the ions reflect from the surface with enough energy to escape over the barrier, so that they desorb directly after the first impact, with a yield almost independent of the surface temperature. Fitting this yield to a simple model gives estimates for the probability for an electron to jump from the incoming atom to the surface as this probability varies with the distance of their separation. When beams of molecules (He, Ar, H₂, N₂, and SF₆) from a nozzle at room temperature strike a Pt surface, initially also at room temperature, they bring in enough energy to increase the temperature of the surface, as measured by a thermocouple, by as much as 50 K. The largest increases occur for the heavy gases Ar and SF₆ when they are seeded into a lighter carrier gas (He). The measured profiles can

be modeled by taking different accommodation coefficients for the two gases.

**University of California
Davis, California 95616**

191. Laser Studies of the Dynamics of Free Radical Reactions

W.M. Jackson \$60,000
Department of Chemistry

Rate constants are measured for a series of CN reactions with saturated hydrocarbons. These rate constants are found to increase with the number of carbon atoms in the hydrocarbon to rates that are near ion-molecule reaction rates. Temperature dependence studies on these reactions are performed such that the activation energy and Arrhenius A factors are obtained. Theoretical calculations are used to relate the overall collision cross section to the long-range attractive potential of dipole-induced dipole and dispersion forces and to the formation of an orbiting complex that enhances the probability of the reaction. The experimental facilities now include a transient infrared spectrophotometer that is being developed to collect infrared emission from CH₃ and CO radicals prepared by ultraviolet laser photolysis of suitable precursors.

**University of California
Irvine, California 92717**

192. Laser Studies on Internal State Dependence of Excitation and Deexcitation Processes

J.J. Valentini \$25,903
Department of Chemistry

Focus is on the elucidation of the vibrational and rotational structure and dynamics of electronically excited states of polyatomic molecules that are important in combustion. Of particular interest is the effect of vibrational and rotational excitation on the state-to-state intramolecular dynamics and the bimolecular quenching and reactions. The project objective is to develop optical spectroscopic methods for detecting important transient species in combustion media, and to provide the spectroscopic data necessary for the analysis of spectra of these species to reveal concentration and temperature information. Various laser spectroscopic methods are used for this work, including laser-induced fluorescence, coherent Raman spectroscopy, and multiple photon ionization. Current studies involve polyatomic free radicals, such as HCO, that are key species in hydrocarbon combustion.

**University of Chicago
Chicago, Illinois 60637**

193. Quantum Dynamics of Fast Chemical Reactions
J.C. Light \$80,000
James Franck Institute

The current objectives of this research are the quantum formulation and exact evaluation of thermal rate constants via an L² implementation of the flux-flux autocorrelation function approach. A full (three-dimensional) discrete variable representation in symmetry adapted (D_{3h} for H₃, C_{2v} for HD₂, and so forth) hyperspherical coordinates permits an easy evaluation of

the flux operator and, we believe, an accurate sequential evaluation of the (L²) eigenvalues of the Hamiltonian in an interaction box. This will permit full evaluation of k(T) as a function of the temperature and perhaps also the exact quantum state-to-state rate constants. One- and two-dimensional studies have been completed with promising results, and work on the three-dimensional problem is well under way.

**University of Colorado
Boulder, Colorado 80309**

194. Laser Photoelectron Spectroscopy of Ions
G.B. Ellison \$100,000
Department of Chemistry

This project involves the spectroscopic study of ions and radicals that may be reactive intermediates in combustion processes. Mass-selected ion beams are prepared and crossed with the output of a CW ArII laser operating on a single line ($h\nu = 488$ nm). The laser detaches electrons from the negative ions, and the kinetic energy of the scattered electrons is monitored with a pair of hemispherical analyzers. A number of silicated ions and sulfur-stabilized anions have recently been investigated. For example, the photoelectron spectrum of the thioformaldehyde negative ion, CH₂S⁻, has been observed and the electron affinity measured: EA(CH₂S) = 0.465 ± 0.023 eV. A geometry for the CH₂S⁻ ions has been determined from an analysis of the photo-detachment Franck-Condon profile. CH₂S⁻ is a planar, C_{2v} species with a C-S bond length of 1.72 ± 0.02 Å. The vibrational frequency for the negative ion C-S stretch is $\nu_3 = 860 \pm 220$ cm⁻¹, while the frequency of the CH₂S⁻ umbrella mode is $\nu_4 = 450 \pm 120$ cm⁻¹. These experimental findings are in excellent agreement with a PNO-CEPA *ab initio* calculation of the thioformaldehyde ion's geometry and electron affinity.

195. Time-Resolved Studies of Free Radicals and Laser-Initiated Chain Reactions
S.R. Leone \$90,000
Department of Chemistry and Biochemistry

A time-resolved Fourier transform infrared (FTIR) emission experiment has been developed for the study of photofragmentation and chain reactions by uniting a commercial FTIR spectrometer with a high-repetition rate laser. High-resolution emission spectra from excited molecular and radical fragments are recorded at time delays down to a few microseconds after the laser pulse. Internal state distributions have been characterized for the HF product from chloro-fluoro-ethylene, CCH from acetylene, and CO from acetone. The dynamics of these decomposition processes are also explored. A new version of the apparatus will obtain time resolutions of 10 nanoseconds for the study of chain reaction systems.

**Columbia University
New York, New York 10027**

196. Energy Partitioning in Elementary Gas-Phase Reactions
R. Bersohn \$80,000
Department of Chemistry

Elementary gas-phase reactions, both bimolecular and unimolecular, are being studied by laser generation of reactants and laser-induced fluorescence detection of the reaction products.

Bimolecular reactions of particular interest have been hydrogen atom exchanges with deuterated molecules such as D_2 , deuterated hydrocarbons, and silane. The energy of hydrogen atoms generated by photodissociation can be varied in the 1 to 4 eV range by changing the wavelengths of light or the target molecule. The cross sections and product translational energies are obtained as a function of energy for the exchanges $H + RD \rightarrow RH + D$. The dynamics of the reaction $H + HCN \rightarrow H_2 + CN$ have been studied from both directions. The CN product is rotationally cold which shows that the transition state is linear. Hydrogen atoms produced by photodissociation of H_2S have a fairly sharp energy distribution. By studying the Doppler-broadened shape of the hydrogen atom absorption as a function of pressure of inert bath gas, the time dependent speed distribution, $f(v,t)$, can be extracted. An important comparison can be made with the solutions of the Maxwell-Boltzmann integrodifferential equation for the same systems.

Cornell University Ithaca, New York 14853

197. *The Detection of the Ethynyl Radical for Studies of the Chemistry of Soot Formation in Hydrocarbon Combustion*

T.A. Cool **\$82,000**
School of Applied and Engineering Physics

A better understanding of the reaction mechanisms by which soot and toxic aromatic compounds are formed in hydrocarbon combustion depends on the development of suitable methods for monitoring trace concentrations of several key radical intermediate species. The goal of this research is the application of a new laser-based technique to this task. Resonance-enhanced multiphoton ionization spectroscopy (REMPI) is capable of the detection of combustion radicals at the part-per-million level. Widespread application of REMPI for flame diagnostics is presently limited by a scarcity of spectroscopic data for Rydberg electronic states of several key combustion radicals. A systematic search for REMPI spectra for excitation of the $3s^211$ and $3p\sigma^211$ Rydberg states of the ethynyl radical, C_2H , is in progress. In the course of this work, a new electronic state in the C_2 radical has been identified. Thirteen vibronic bands assigned to the two-photon $1^1\Delta_u \leftarrow A^1\Pi_u$ transition have been observed by REMPI spectroscopy for laser wavelengths ranging from 370 to 480 nm. Accurate spectroscopic constants have been obtained for the previously unobserved $1^1\Delta_u$ state. Work has been completed on the REMPI spectroscopy of the $3p^211$ Rydberg state of the HCO radical which has resulted in the first laser-based *in situ* monitoring of HCO profiles in hydrocarbon flames.

198. *State-Resolved Studies of the Methyl Radical* P.L. Houston **\$95,000** Department of Chemistry

The three-dimensional velocity distribution of the methyl radical prepared by the photodissociation of precursor molecules, such as methyl iodide, is measured in selected vibrational and rotational states via multiphoton ionization. The velocity distribution of the fragments is determined directly from the arrival time of the CH_3^+ ions, the relative timing of lasers and gates, and the location of the impact of the CH_3^+ on the detector. The correlation between the recoil vector v and the angular momentum vector J of the fragments is also determined from

the doppler profiles of parallel and perpendicular, high-resolution, vibration-rotation spectra from which properties of the potential surface (along with the methyl iodide dissociated) are inferred. Using these techniques, the reactions of methyl radicals with oxygen molecules and of methane with hydrogen atoms are under investigation.

Emory University Atlanta, Georgia 30322

199. *Theoretical Studies of Combustion Dynamics* J.M. Bowman **\$75,000** Department of Chemistry

The project objective is to develop and apply theoretical methods to treat fundamental collisional processes of basic importance in combustion. The two areas of current interest are recombination reactions and bimolecular exchange reactions. In the former area, the $H + CO$ system (which can recombine in the presence of a third body to form HCO) is under investigation. Large-scale coupled-channel scattering calculations (using an *ab initio* potential) are being conducted on a CRAY 2 supercomputer and on an IBM 3090. Of particular interest are the low-energy, thermally accessible resonances in this system and the high-energy collisions. These studies will be extended to explore alignment effects in this system. In the area of bimolecular exchange reactions, an approximate quantum theory has been developed and applied very successfully to the $O(^3P) + H_2$, D_2 , and HD reactions, using an *ab initio* potential. A study of the $OH + H_2$ reaction using this theory and a semi-empirical potential surface has been initiated. Computational studies of the vibrations of interesting polyatomic systems such as H_2O and H_2CO will be performed as potential surfaces become available for them.

University of Georgia Athens, Georgia 30602

200. *Potential Energy Surfaces for Chemical Reactions* H.F. Schaefer **\$90,001** Department of Chemistry

In recent years theoretical chemistry has become a significant source of broad generalities and 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. Using *ab initio* quantum mechanics, reactions being studied 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, and the nature of hydrated hydronium clusters.

Georgia Institute of Technology
Atlanta, Georgia 30332

201. Reactive Collisions of High-Temperature Systems

M.M. Graff
School of Physics

\$81,901

A neutral beam apparatus is being developed to study reaction dynamics of neutral systems whose endothermicities or activation barriers preclude study by molecular beam techniques. The experiment will investigate the dependence of reactivity on collision energy and on molecular internal energy. Systems to be studied initially include the basic oxygen-hydrogen combustion systems $O + H_2 \rightarrow OH + H$ and $OH + H_2 \rightarrow H_2O + H$. The experiment is based on a double mass spectrometer design, modified for the study of neutral species. Production of a velocity- and mass-selected beam of radicals will be effected by photodetachment of the corresponding negative ion with a large-frame argon ion laser. The influence of H_2 rotational energy will be studied by comparing results for para- and normal hydrogen at low temperature. The structure of the excitation function will be observed for the entire range of chemically interesting collision energies.

Harvard University
Cambridge, Massachusetts 02138

202. Fundamental Studies of Carbenes and Hydrocarbon Radicals

P. Thaddeus, C. Gottlieb
Division of Applied Sciences

\$68,000

This project emphasizes fundamental millimeter-wave spectroscopy of the carbenes, carbon chain radicals, and ring-chain hybrids, nearly all of which are involved in reactions of hydrocarbon combustion. The investigation will be made with the spectrometer successfully used for the first laboratory detection of a number of carbon chain radicals and the small carbene ring cyclopropenylidene (C_3H_2). The project stresses wide searches in frequency, which will allow the study of reactive species present in both nonaromatic and aromatic sooting fuels (e.g., acetylene, allene, 1,3-butadiene, benzene, toluene, and so forth). An advantage of millimeter-wave over other wavelength regions is that, owing to high symmetry, fuels such as acetylene, allene, and benzene have no permanent electric dipole moments and therefore no interfering transitions. The formation of cyclopropenylidene at high concentrations in the nonaromatic fuels acetylene and allene, suggests the presence of other carbene rings including cyclopentadienylidene, cycloheptatrienylidene, and phenyl carbene. Examples of nonaromatic carbenes proposed for study are vinylidene, methyl carbene, propargylene, propadienylidene, vinylmethylene, butatrienylidene, and ethynylvinylidene.

Howard University
Washington, District of Columbia 20059

203. Photolytic Processes for Measurement of Combustion Heats of Formation and Reaction Rates

J. Halpern, H. Okabe
Department of Chemistry

\$55,000
(24 mo.)

Alkoxy radicals, RO ($R = CH_3O$, C_2H_5O , $i-C_3H_7O$, and $t-C_4H_9O$), are important species in the combustion of hydrocarbons. This project includes measurements of their kinetics, fluorescence spectra, and thermochemistry. For kinetics, RO radicals were produced by the laser photolysis of RONO at 355 nm and followed by the time-dependent decreases of RO laser-induced fluorescence at 337 nm. Rate constants for quenching of the excited radical, whose collision-free lifetime is 0.64 ± 0.09 microseconds, with NO and O_2 have been determined. Further measurements have been made of fluorescence spectra of the CH_3O , $n-C_3H_7O$, and $t-C_4H_9O$ radicals. To determine the heats of formation of the alkoxy radicals, the threshold for production of excited RO from the photolysis of RONO is being measured. The tunable light at about 200 nm is produced by Raman shifting doubled Nd-YAG pumped dye laser light. First measurements with C_2H_5O show a threshold above 215 nm. A laser photolysis/ESR apparatus has been set up to detect complex gas-phase free radicals following laser photolysis.

University of Illinois
Chicago, Illinois 60680

204. Kinetics of Elementary Atom and Radical Reactions

R.J. Gordon
Department of Chemistry

\$86,000

The project objective is to study the chemical reactions and vibrational energy transfer rates of small molecules. Emphasis is on (1) the kinetic isotope effects in the reaction of ground state oxygen atoms with hydrogen molecules and (2) the use of time-resolved optoacoustics to measure the vibrational relaxation rate of very highly excited molecules. In the first area the temperature dependence of the reactions of oxygen atoms with H_2 , D_2 , and HD has been measured. Both the intermolecular isotope effect for H_2 and D_2 and the intramolecular isotope effect for HD are in excellent agreement with theory, but only if tunneling is taken into account. This is the first quantitative demonstration of a large tunneling effect in gas phase reactions above room temperature. Measurements based on the optoacoustic effect take advantage of the relationship of the shape of the acoustic waves produced in a nonresonant cavity to the relaxation time of the gas. A simple exponential decay has been observed in the relaxation of large molecules such as SF_6 and C_6F_5H . For SiF_4 , however, nonexponential behavior has been observed that may indicate bottleneck effects in intermediate-sized molecules. This method has also been used to study the relaxation of CH_3Cl and CH_3Br at low energies, where a surprisingly fast decay has been observed, ruling out a rotational bottleneck and suggesting that the mechanism may be more complicated than previously thought.

- 205. Shock Tube Studies of High-Temperature Hydrocarbon Pyrolysis Kinetics**
J.H. Kiefer \$94,000
Department of Chemical Engineering

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 gradient (net endothermic rate) and a 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 now confirmed the rate and mechanism for 1,3-butadiene dissociation. A study of the dissociation of vinylacetylene has led to the proposal of a new carbene insertion mechanism for acetylene polymerization, and this mechanism has now been employed in a successful modeling of previous shock tube data on this reaction.

Illinois Institute of Technology
Chicago, Illinois 60616

- 206. Studies of Combustion Kinetics and Mechanisms**
D. Gutman \$145,000
Department of Chemistry

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 1,000 K) and pressure (1 to 20 torr), and the 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., $\text{CH}_3 + \text{CH}_3$), reactions of free radicals with atomic oxygen (e.g., $\text{O} + \text{C}_2\text{H}_5$ and $\text{O} + \text{C}_3\text{H}_5$), and reactions of these same free radicals with molecular oxygen (e.g., $\text{C}_2\text{H}_5 + \text{O}_2$). 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 Iowa
Iowa City, Iowa 52242

- 207. Determination of Step-Size Parameters for Intermolecular Vibrational Energy Transfer**
D.C. Tardy \$78,899
Department of Chemistry

Intermolecular vibrational energy transfer for highly excited polyatomic molecules is involved in any mechanism in which excitation energy is required (pyrolysis) or in which energy must be removed from a hot source (cooling). The average energy removed per collision, $\langle \Delta E \rangle$, is a useful quantity to compare efficiency for energy transfer. The objectives of this work are: (1) to determine the dependence of $\langle \Delta E \rangle$ on excitation energy and on the molecular complexity (number of vibrational modes) of substrate and deactivator; (2) to assess the importance of intermolecular attractions (complex formation) on vibrational energy transfer; and (3) to obtain detailed information on the energy distribution after collision and to evaluate the importance of $\langle \Delta E \rangle$ on high temperature unimolecular reactions. This information will be obtained by monitoring the time dependence of the infrared emission, ultraviolet absorption, refractive index, and pressure. The results from these complementary techniques will be benchmarked with $\langle \Delta E \rangle$ values from previous studies on the relaxation of chemically activated alkyl and fluoroalkyl radicals. Trajectory calculations simulating energy transfer are being performed for generic substrate/deactivator pairs to provide additional details and insight on the important parameters. Model calculations are also being performed to determine the feasibility of obtaining $\langle \Delta E \rangle$ information from experimental data for high-temperature unimolecular reactions.

Jackson State University
Jackson, Mississippi 39217

- 208. Infrared and Visible Laser Double Resonance Studies of Vibrational Energy Transfer Processes in Polyatomic Molecules**
R. Bhatnagar \$47,075
Department of Chemistry

The excitation spectra of selected compounds are monitored in the presence of vibrationally and electronically excited energy-donor compounds from which the rotational and vibrational energy level distributions at thermal equilibrium are inferred. Energy-donor compounds are prepared in excited electronic or vibrational energy states by laser irradiation and transfer their excess energy to the studied compounds. The rotation and vibration dependence of the energy transfer are determined from the changes in the excitation spectra. Measurements are made as functions of pressure, degree of excitation of the energy-donor compounds, and time between excitation of the energy-donor compounds and measurement of the fluorescent signal. The species under study include propynal (HCCCHO) and glyoxal (CHOCHO), and energy-donor compounds include SF_6 and CH_3F .

University of Kentucky
Lexington, Kentucky 40506-0055

- 209. Laser Spectroscopy and Dynamics of Combustion Intermediates**
D.J. Clouthier **\$56,085**
Department of Chemistry

The spectroscopy and excited-state dynamics of sulfur-containing polyatomic species that are of interest in combustion chemistry are under investigation. The $S_1 \leftarrow S_0$ spectrum of S_2O has been obtained under supersonic jet conditions and vibronically analyzed. Using a newly designed high-temperature pyrolysis jet, rotationally resolved LIF spectra of H_2CS have been recorded at rotational temperatures of 5 to 10 K. Collision-free, single rotational level lifetimes of thioformaldehyde vapor have been measured; and long (150 to 300 μsec) rotational level dependent lifetimes have been found. Relative fluorescence quantum yield measurements have shown that levels coupled to S_0 or T_1 have longer than purely radiative lifetimes because of dilution of the S_1 oscillator strength. In continuing studies of the spectra of new free radicals, a new transient spectrum in the 750 to 850 nm region has been observed, which is likely to be that of C_2S . Experiments are in progress to establish more firmly the identity of the carrier of the spectrum.

University of Massachusetts
Amherst, Massachusetts 01003-0035

- 210. Theory of the Dissociation Dynamics of Small Molecules on Metal Surfaces: Finite Temperature Studies**
B.E. Jackson **\$32,619**
Department of Chemistry

Realistic quantum mechanical models are being developed for studying the dissociative adsorption of small molecules on metals. Time dependent techniques are used where the molecular wave function is evolved in time and reacted with the metal. The first quantum study of dissociative adsorption has recently been implemented, using an exact solvable two-dimensional model. The dissociative sticking probability has been computed for H_2 and its isotopes on Ni, as a function of molecular kinetic energy. A comparison has been made between classical and quantum studies of dissociation. Techniques have been developed that extend these time dependent theories to finite surface temperature, with only a small increase in computer time. This allows for energy exchange with the vibrations of the solid, which are treated in a fully quantum fashion. Six dimensional quantum models for the dissociative adsorption of diatomics are now being examined. They will be used to compute dissociative sticking probabilities for several diatom-metal systems, as a function of molecular kinetic energy, rotational and vibrational state, and angle of impact. The influence of various features of the gas-surface interaction potential will also be examined. With the inclusion of finite temperature, a complete comparison with experiment will be possible.

Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

- 211. Aromatics Oxidation and Soot Formation in Flames**
J.B. Howard **\$102,000**
Department of Chemical Engineering

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 and soot particle size and number concentration through the reaction zone of low-pressure one-dimensional flames. The oxidation of benzene and other aromatic compounds with hydroxyl radical and oxygen atom 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, are being used to study gases including high molecular weight compounds. Soot particles are being studied by optical scattering and absorption measurements in the flame and electron microscope analysis of molecular-beam deposits. 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 1,000 amu and larger, containing alkyne, alkene, and alkane structures.

- 212. Spectroscopic and Dynamical Studies of Highly Energized Small Polyatomic Molecules**
R. Silbey, R.W. Field **\$137,000**
Department of Chemistry

The pure sequence spectra of highly excited ground state acetylene (C_2H_2) have been studied using stimulated emission spectroscopy (SEP). Statistical measures must be used to extract dynamical information from these spectra because of their complexity. Two such tests have been applied. The first is the calculation of the average of the square of the Fourier transform of the spectrum $\langle |F[I(\omega)]|^2 \rangle$, which focuses on the short time dynamics. The second is a cross correlation of two SEP spectra originating from (vibrationally) maximally different intermediate levels belonging to the same rigorous quantum numbers, which offers a way of studying the decay of specific spectroscopically defined localized excitations. These techniques have provided evidence of the structural isomer vinylidene (H_2CC) and information about the energy and lifetime of its vibrational levels. In addition, recurrences in the Fourier transform of the acetylene SEP spectrum at a vibrational energy of 26,000 cm^{-1} above the ground state may be indicative of H orbiting CCH. Experiments are under way to test this interpretation.

University of Michigan
Ann Arbor, Michigan 48109

- 213. Energy-Transfer Properties and Mechanisms**
J.R. Barker \$99,000
Department of Atmospheric, Oceanic, and Space Sciences

This project studies the mechanisms and properties of 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, time-dependent thermal lensing and time- and wavelength-resolved infrared fluorescence are used to monitor the vibrational energy in excited molecules prepared by pulsed laser excitation. In order to determine the mechanisms of energy transfer, isotopically substituted isomers are investigated to determine the effects of dipole moments, symmetry properties, fundamental vibrational frequencies, and so forth. In the theoretical effort, improved models are being developed of internal state densities and of the infrared emission from highly excited molecules. In addition, collisional/reaction master equation calculations are being used both to model the experiments and to investigate the manifestations of energy transfer under extreme conditions. Also under development is a new version of unimolecular rate theory (termed "spectroscopic RRKM theory") that uses detailed spectroscopic data for the decomposing molecule, instead of the usual estimated transition-state parameters.

University of Minnesota
Minneapolis, Minnesota 55455

- 214. State-to-State Dynamics of Molecular Energy Transfer**
W.R. Gentry, C.F. Giese \$102,000
Departments of Chemistry and Physics

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 excitation of polyatomic molecules in collisions with atoms. Previous experiments have established that certain specific modes of vibration are excited selectively, even when many other modes are energetically accessible. Further exploration of this mode selectivity is now being pursued by detailed examination of the rotational excitation which occurs concurrently with vibrational excitation, with the expectation that the rotational state distribution contains information about which collision geometries lead to a high probability of exciting a particular vibrational mode.

- 215. Variational Transition State Theory**
D. Truhlar \$83,000
Department of Chemistry

This project is concerned with the development and applications of generalized transition state theory and multidimensional tunneling approximations to chemical reaction rates. Several practical versions of variational transition state theory (VTST) have been developed and implemented, namely canonical variational theory (CVT), improved canonical variational theory (ICVT), and microcanonical variational theory (μ VT). Several accurate multidimensional semiclassical tunneling approximations have also been developed and implemented. 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. The goal is to develop accurate methods for calculating chemical reaction rate constants that remain practical even for reasonably complicated molecules. The approximations mentioned above yield rate constants for systems whose potential energy surface is known or assumed. Another important aspect of this work is the determination or modeling, semiempirically and/or from electronic structure calculations, of potential energy surfaces. New flexible procedures for representing the potential surfaces of reactive systems by global and semiglobal analytic functions have been developed and implemented. Finally, a new initiative is concerned with including variational and tunneling effects in a thermochemical data base.

National Bureau of Standards
Gaithersburg, Maryland 20899

- 216. Laser Studies of Chemical Dynamics at the Gas-Solid Interface**
R.R. Cavanagh, D.S. King \$78,000
Center for Chemical Physics

Quantum state specific laser diagnostics applied to the question of energy transfer at surfaces provides the focus of the present research. Primary consideration is given to thermally activated desorption and the importance of nonthermal desorption channels. In thermally activated desorption, it has been found that the internal state distributions consistently resemble Boltzmann (i.e., thermal) distributions, but that the temperature of these distributions does not always show complete accommodation with the surface. Recent experiments have probed the role of laser-induced surface heating. Although the calculated temperature peak achieved in these experiments was typically 320 K, LIF data indicated that a significant fraction of the desorbed molecules escaped through a nonthermal channel. The wavelength dependence of this laser-induced desorption process has recently been examined. These data show that the desorption dynamics is not the result of an adsorbate localized excitation process, but reflect the optical generation of hot electrons in the near-surface region of the metal. Current work is also directed at establishing the role of negative ion resonances in the desorption process. These studies will induce desorption using both a wider range of excitation wavelengths and picosecond pulse durations.

217. Kinetics Data Base for Combustion Modeling
J.T. Herron \$95,000
Center for Chemical Physics

This project is designed to provide a reliable and consistent set of recommended rate constants for use by modelers, chemical kineticists, and theoreticians. The focus is on the elementary single-step thermal reactions relevant to the combustion of organic compounds. The first reactions evaluated were those involving the C1 through C4 aliphatic compounds and their related radicals, and the reactions of atomic oxygen. This work is being published in the *Journal of Physical and Chemical Reference Data*. In addition, compilations were published that include data on over 2,500 reactions, and which cover a broader range of reactions than those included to date in the evaluations. These data are now part of a searchable PC data base covering the literature from 1971 to 1985. Additional data are being added continuously. Over the past year work was completed on the alkanes and their radicals, and work was initiated on the chemistry of unsaturated species. Current activities involve the further expansion of the work on unsaturates with the evaluation of data on the reactions of trans-2-butene and the allyl radical. It is planned to continue to extend the data base to include alkynes and aromatic and heterocyclic species.

University of New Orleans
 New Orleans, Louisiana 70148

218. Identification and Temporal Behavior of Radical Intermediates Formed During the Combustion and Pyrolysis of Gaseous Fuels
R.D. Kern, Jr. \$70,000
Department of Chemistry

This project is concerned with the mechanisms of soot formation in flames as elucidated by the pyrolysis of hydrocarbon fuels. Analysis of the reflected shock zone by time-of-flight mass spectrometry for the high-temperature pyrolyses of C₃H₄, 1,2- and 1,3-C₄H₆, C₄H₄, C₂H₂, and C₅H₅N revealed amounts of benzene that were comparable to the soot yields obtained by other workers using the laser extinction techniques. In those systems where comparable mixtures were investigated, it is apparent that the relative magnitudes of benzene production are of the same order as the soot yields; namely, allene > 1,3-butadiene > vinylacetylene ≈ acetylene > pyridine. The benzene concentration curves for each fuel exhibit bell shapes similar to the sooting tendency profiles. The benzene maximum for each fuel after one millisecond reaction time precedes the respective soot yield maximum with respect to temperature. Furthermore, at the respective benzene maxima, the corresponding soot yields for each fuel are exceedingly low. A correlation has been found between the concentration profile of a readily observable molecular species, benzene, and the bulk observable of soot yield. Benzene production is an excellent diagnostic of soot formation since those fuels that produce small amounts of benzene also have low soot yields. Fuels that exhibit substantial benzene concentrations have high sooting tendencies.

State University of New York/Bufalo
 Buffalo, New York 14260

219. Multiphoton Interactions in Molecules with Picosecond Laser Pulses
H.-S. Kwok \$71,000
Department of Electrical and Computer Engineering

Picosecond dye laser and infrared laser pulses are used to measure the process of intramolecular energy transfer in polyatomic molecules. A narrow tunable dye laser excites the molecule into specific vibrationally resolved electronic excited states. The redistribution of energy from those states is monitored by nonresonant multiphoton ionization. During the past year, it was found that the rate of internal energy conversion from the electronic excited state B₁ to the ground vibrationally excited state A₁^{*} is very dependent on the vibrational energy content of the pumped state. Rates ranging from 6 ns to less than 30 ps were measured in CrO₂Cl₂. Various vibrational progressions in the B₁ state were studied, with similar results. The effects of collisions and the laser polarization on the energy-transfer mechanism were also investigated. Other molecules such as azulene are currently under study. In addition to the investigation of internal energy conversion, this method can be used to measure the rate of energy transfer between specific vibrational states by using a tunable infrared laser pulse.

State University of New York/Stony Brook
 Stony Brook, New York 11794

220. Multiphoton Ionization Spectroscopy and Photochemistry of Transient Species
P.M. Johnson \$75,884
Department of Chemistry

Resonance ionization spectroscopy is found to be a valuable tool for the investigation of optical transitions of molecules (including metastables and radicals) that are not seen using conventional techniques. New transitions give us additional information about the excited-state electronic structure of both familiar and unstable molecules. These transitions are achieved by preparing the molecules in excited states which act as initial levels for resonance ionization spectroscopy, and by using multiphoton transitions from ground electronic levels. Normally the species under study is entrained in a supersonic beam, providing a collisionless and cold environment. Interesting molecules are created in the supersonic beam by means of a pulsed electric discharge or a pyrolysis region at the exit of a pulsed valve. The discharge is a bountiful source of excited metastable states and radicals, creating for study the excited states of nitrogen, carbon monoxide, and benzene and the ground state of CCl radical. We have been able to dramatically expand the knowledge of the CCl radical electronic structure. A multiphoton ionization study of the iodine molecule has revealed several new excited states that have interesting dissociation dynamics in competition with the ionization.

University of North Carolina
Chapel Hill, North Carolina 27514

221. *PEPICO Studies of Ion Dissociations: The Structure and Heats of Formation of Ions, Molecules, and Free Radicals*
T. Baer \$95,000
Department of Chemistry

This research is concerned with the development of photoelectron-photoion coincidence (PEPICO) spectroscopy and its application to two classes of compounds: fused rings and organic radicals. In the PEPICO technique, ions are generated by photoionization and detected in delayed coincidence with energy selected electrons. Ions are thus prepared with selected, known internal energies allowing the study of (1) the role of internal energy in the dissociation of metastable ions, (2) the manner in which internal energy is distributed in the products of dissociation, and (3) under certain conditions, the dynamics of dissociation. Fused ring compounds are vaporized and expanded in a supersonic nozzle to reduce the internal energy of the molecules so that the onset of ionization can be measured with a precision comparable to the resolution of the instrument. The heats of formation and ionization potentials of the parent ion and of the remaining fragments are determined from the photoionization energies, the energies of photodissociation fragments, and the ionization potentials and heats of formation of some of the fragments.

University of Pennsylvania
Philadelphia, Pennsylvania 19104

222. *Dynamics of Vibrationally Excited Polyatomic Molecules and Their Unstable Isomers on the Electronic Ground State Potential Surface*
H.-L. Dai \$96,225
Department of Chemistry

The stimulated emission pumping (SEP) technique has been used to study the high vibrational levels of the methylene radical, an important species in energy-related chemistry. The short lifetime and the low concentration of radicals in most chemical environments make their spectroscopic study very difficult, particularly for excited vibrational levels. With short laser pulses, SEP should be sensitive enough for the study of the short-lived radicals. As a first demonstration, the $\nu_2 = 3$ level of the methylene radical singlet ground state has been studied. The spectroscopic data allow the determination of the vibrational energy and the rotational constants of the ν_2 bending levels, which in turn are used to characterize the double-minimum bending potential. Many problems associated with the triplet state, such as the singlet-triplet splitting and the singlet-triplet coupling, can be investigated with much more detail and accuracy with the SEP technique. In addition to vibrational spectroscopic information, SEP can be used to excite a large quantity of radicals into a selected high vibrational level. The effect of vibrational excitation on radical reactions can then be investigated. In a separate experiment, the dissociation behavior of vibrational levels near the dissociation barrier in the formaldehyde molecule has been studied using Stark Level-Crossing Spectroscopy, and the dissociation rate of single electronic ground-state, vibration-rotation levels at $28,300 \text{ cm}^{-1}$ has been measured. The rates vary over two orders of magnitude for a group of quasi-degenerate levels within a 0.1 kcal/mole range.

These experiments reproduced the results from a theoretical calculation that predicted the variation of the dissociation rates based on limited coupling among the vibrational modes.

223. *Half-Collision Studies of Inelastic Energy Transfer Processes*
M. Lester \$95,000
Department of Chemistry

The focus of this project is the investigation of inelastic half-collisions between molecules. This is accomplished by aggregating a collision pair in a van der Waals (vdW) complex and then studying the photodissociation dynamics of the complex. Currently, the half-collision dynamics between rare gases and hydroxyl radicals are being examined at the state-to-state level of detail. The collision pair is selectively prepared in a metastable state having an internal energy content in the OH moiety which exceeds the vdW bond strength. Energy transfer to vdW vibrational motions results in rupture of the weak vdW bond. The inelastic scattering process that occurs as the OH and rare gas species separate is detected by probing the final state distribution of the OH fragments. This half-collision approach promises to reveal a state-specific picture of the intermolecular potential responsible for inelastic energy-transfer processes.

University of Pittsburgh
Pittsburgh, Pennsylvania 15260

224. *Quantum State Resolved Desorption of CO from Solid Surfaces*
K.C. Janda \$86,000
Department of Chemistry

This research is designed to characterize the dynamics of CO deposited on and desorbed from surfaces. The rotation-vibration energy distribution of CO desorbed from surfaces is measured using multiphoton ionization techniques. The CO is thermally desorbed from a Ni(111) surface using both a programmed temperature rise and by rapid, pulsed laser heating. CO arising from associative desorption of carbon and oxygen atoms from surface-adsorbed carbon and oxygen atoms is also under investigation. In addition, the state distribution of CO liberated by photoreaction of surface adsorbed molecules containing CO, in particular $\text{Fe}(\text{CO})_5$ and formaldehyde, is measured and compared with that of CO deposited alone on a surface.

Princeton University
Princeton, New Jersey 08544

225. *Comprehensive Mechanisms for Combustion Chemistry: An Experimental and Numerical Study with Emphasis on Applied Sensitivity Analysis*
F.L. Dryer \$98,451
Department of Mechanical and Aerospace Engineering

The experimental aspects of the project are conducted in a flow reactor facility that permits chemical kinetic observations at atmospheric pressure (at about 850 K to 1200 K) and for reaction times the order of 10 to 1000 msec. Sampling of stable reactant, intermediate, and product species concentrations provides substantial definition of the phenomenology of reaction mechanisms and a much more constrained set of pure kinetic informa-

tion than can be derived in flames, or shock tubes. The modeling aspects of the project emphasize (1) the use of hierarchical mechanistic construction as a means of developing kinetic mechanisms and (2) the comparison of model and experiment using elemental gradient sensitivity based techniques. Modeling using a well-defined and validated mechanism for the CO/H₂/O₂ system and perturbations of experimental oxidations by small amounts of additives is also used to derive absolute reaction rates and to investigate the compatibility of elementary kinetic rate information. Chemical issues of particular interest continue to include the CO/H₂/O₂ system and its perturbation by added species (to obtain elementary kinetic data involving a small amount of an added hydrocarbon), the formaldehyde pyrolysis and oxidation systems, the acetaldehyde pyrolysis and oxidation systems, and the pyrolysis and oxidation mechanisms of simple alcohols.

226. Aromatic-Radical Oxidation Kinetics
I. Glassman, K. Brezinsky **\$79,980**
Department of Mechanical and Aerospace Engineering

The focus of this project is on elucidating the role that the oxygen atom plays in the oxidation of aromatic compounds. During this past year, three phases of the project have been completed: two studies of the perturbing effect of NO₂ addition to the oxidation of benzene and toluene, and a study of the pyrolysis of phenol. When NO₂ is added to the flow reactor oxidation of benzene, the rate of decay of benzene and the formation of CO and C₂ products is increased, but the production of phenol and cyclopentadiene is virtually eliminated by the removal of oxygen atoms through the fast reaction of hydrogen with NO₂. The increased overall rate of reaction results from an increased OH concentration that leads to an increased rate of benzene + OH to form H₂O and phenyl, which then rapidly reacts with O₂. The addition of NO₂ to the oxidation of toluene causes the toluene to be consumed faster and the concentrations of carbon monoxide, benzaldehyde, benzene, methane, C₂'s and C₄'s to increase while the cresols, phenol, and cyclopentadiene concentrations are reduced. These experimental observations result from a reduction in the concentration of hydrogen and oxygen and an increase in OH radical caused by the reaction of hydrogen and NO₂. The experiments also confirm that the primary source of the phenoxy radical is the unusual chain branching reaction of phenyl and molecular oxygen. From the study of the pyrolysis of phenol, major species profiles are obtained for carbon monoxide, cyclopentadiene, and benzene. A chemical mechanism has been developed and integrated numerically to generate carbon monoxide, cyclopentadiene, and benzene profiles that match well those obtained experimentally.

227. Dynamics and Kinetics of Molecular Systems
H.A. Rabitz **\$132,047**
Department of Chemistry

This project has two phases consisting of studies in molecular dynamics and chemical kinetics. The first phase of the research in collision dynamics concerns understanding the relationship between the structure of potential surfaces and resultant features in observable cross sections and rate constants. This research has been extended further to the electronic level of probing to study how orbital structure manifests itself in dynamical observables. Techniques from both quantum mechanics and classical dynamics are being used in this work.

The second phase of the research is concerned with the development and application of sensitivity analysis tools for the understanding of complex chemical mechanisms. Both time- and space-dependent problems are under study with emphasis on combustion phenomena. Sensitivity analysis is being developed for probing the role of rate constants, transport coefficients, initial conditions, and boundary conditions on laboratory observables. The ultimate aim of all aspects of the research is to understand the interrelationship between a hierarchy of microscopic and macroscopic observables in terms of fundamental interactions.

Purdue University
West Lafayette, Indiana 47907

228. Quenching-Independent Measurement of Species Concentrations in Flames by Laser-Induced Fluorescence
N.M. Laurendeau **\$31,052**
Department of Mechanical Engineering

The primary objective of this research is the development of laser-induced fluorescence methods for measuring the concentrations of flame species, including monatomic and diatomic radicals and polycyclic aromatic hydrocarbons. Development of these methods will result in major advances in combustion diagnostics. An associated, long-term research goal is the development of diagnostic techniques that will provide new understanding of combustion kinetics, the interaction between kinetics and turbulent flow, and the influence of kinetics on the performance and emissions of practical combustion devices. Recent accomplishments include: (1) demonstration of quantitative, laser-saturated fluorescence measurements of both OH and NH concentrations; (2) development of a linear-fluorescence method for analyzing mixtures of polycyclic aromatic hydrocarbons in a vapor cell; (3) demonstration of quantitative, two-photon measurements of atomic hydrogen using photoionization controlled-loss spectroscopy; and (4) development of a temperature measurement technique, using the anomalous fluorescence of pyrene. Current research involves the application of OH and H measurements to the kinetics of soot formation in premixed flames and extension of the laser-saturated fluorescence method to nitric oxide.

Rensselaer Polytechnic Institute
Troy, New York 12180-3590

229. Kinetic Measurements on Elementary Fossil Fuel Combustion Reactions over Wide Temperature Ranges
A. Fontijn **\$77,000**
Department of Chemical Engineering

The goal of this project is to provide accurate data on the temperature dependence of the kinetics of elementary combustion reactions, to gain a better fundamental understanding and predictive ability of the chemistry involved, and for use by combustion modelers. Experimental measurements are made by the high-temperature photochemistry (HTP) technique, which allows observations on single reactions in the 300 to 1,800 K range. This year the study of a series of reactions of oxygen atoms with the C₂ hydrocarbons was completed with measurements on the ethane reaction. The reaction of oxygen atoms

with propylene and 1,3-butadiene was also studied, and a series of measurements begun on the reactions of oxygen and hydrogen atoms with benzene and toluene. Earlier studies of the ethane reaction over more limited temperature ranges showed no deviation from Arrhenius behavior. However, their combination suggested strong deviation and the HTP work has confirmed this. The curvature is stronger than predicted by simple transition state theory (TST), but additional consideration of quantum mechanical tunneling leads to good agreement. Tunneling is also evident in earlier HTP studies of hydrogen-atom transfer reactions. The data on the propylene reaction agree with a simple TST treatment for a single intermediate adduct channel. However, such an expression does not fit the results above 850 K for the ethylene reaction. In the butadiene reaction, a fraction of the oxygen atoms is regenerated. As a result, the rate coefficients in the literature based on oxygen-atom consumption alone are somewhat low.

Rice University Houston, Texas 77005

230. *Infrared Absorption Spectroscopy and Chemical Kinetics of Free Radicals* R.F. Curl, Jr., G.P. Glass **\$75,000** Department of Chemistry

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. Both spectroscopic and kinetic studies are to be conducted. In the former area, the high-resolution infrared spectra of CH_2OH , CH_3O , H_2CCHO (vinoxyl), HCCO (ketyl), and COOH are to be investigated. In the latter area, the kinetics and mechanisms of several reactions of free radicals in combustion are to be investigated using free radicals and atoms produced by excimer laser flash photolysis and monitored by infrared absorption spectroscopy. Focus is on the study of the branching ratios of free-radical reactions as a function of temperature. Currently the room temperature branching ratios into the several thermochemically accessible channels of the $\text{C}_2\text{H} + \text{O}_2$ reaction are under investigation. This work has established that the reaction produces $\text{H} + 2\text{CO}$ and that the channel producing $\text{OH} + \text{CCO}$ is of negligible importance. Quantitative measurement of the $\text{H} + 2\text{CO}$ channel is under way. Branching ratios for the reactions $\text{NH}_2 + \text{NO}$, $\text{O} + \text{C}_2\text{H}_4$, and $\text{OH} + \text{C}_2\text{H}_4$ will be investigated in the future.

231. *Supersonic Bare Metal Cluster Beams* R.E. Smalley **\$89,000** Department of Chemistry

Research into the properties of bare metal clusters has progressed along two major directions over the past year. The first is the study of the surface reactivity of individually mass-selected transition metal cluster ions trapped in the high magnetic field of an ion cyclotron resonance apparatus (FT-ICR) specially developed for the purpose in earlier years of this project. Specifically, the rates and products of H_2 chemisorption on transition metal cluster surfaces have been studied at $>50,000:1$ mass resolution for 2 to 20 clusters of the elements vanadium, niobium, tantalum, cobalt, rhodium, and iridium. Two key results emerging from this FT-ICR work are (1) there is little if any charge-dependence of the reaction patterns, and

(2) cluster shape is often the critical factor. The second area is ultraviolet photoelectron spectroscopy (UPS) of the mass-selected negative ions of cold metal clusters, using a time-of-flight magnetically focused electron spectrometer developed last year. UPS results for copper, silver, gold, and aluminum clusters in the 2 to 40 atom size range have been found to strongly support the near-metallic jellium picture of the electronic structure of these species.

University of Rochester Rochester, New York 14627

232. *Low-Energy Ion-Molecule Reaction Dynamics and Chemiionization Kinetics* J.M. Farrar **\$85,000** Department of Chemistry

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. Emphasis is on studies of proton transfer reactions occurring on double-minimum potential surfaces. By studying proton transfer and isotope exchange collisions and nonreactive energy-transfer collisions in systems such as $\text{OH}^+ + \text{D}_2$, $\text{OD}^+ + \text{NH}_3$, and $\text{OD}^+ + \text{CH}_2=\text{CH}=\text{CH}_2$, 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. To test the theoretical foundations of such collisions, simple diatomic systems such as $\text{Na}^+ + \text{Na} \rightarrow \text{Na}_2(v', J') + e^-$ and $\text{H}^+ + \text{Na} \rightarrow \text{NaH}(v', J') + e^-$ are being examined. Rotational state-resolved detection of the products, using laser-induced fluorescence and multiphoton ionization, will yield the first opacity function measurements for detachment. Experimental methods and theoretical results from the diatomic systems will be applied to examine important combustion related reactions such as $\text{O}^+ + \text{H}_2$ and $\text{O}^+ + \text{C}_2\text{H}_4$.

University of Southern California Los Angeles, California 90089

233. *Reactions of Carbon Atoms Using Pulsed Molecular Beams* H. Reisler **\$102,491** Department of Chemistry

Reaction dynamics of carbon atoms in selected electronic states with various small molecules relevant to combustion systems are studied using crossed, pulsed atomic, and molecular beams. Various photolytic means are used to produce the carbon atoms in well-defined electronic states from precursor molecules. Reactants and products are detected using laser-induced fluorescence or multiphoton ionization. When multiphoton ionization is used as the detection method, the translational energy of the photofragments is determined from the relative times of the photoionization pulse and the ion detection. Both detection techniques are of sufficiently high resolution to obtain the vibrational and rotational energy distributions in product molecules. The reactions of NO , NO_2 , and SO_2 with carbon atoms are currently under investigation, and for each of the reactions studied, the branching ratios between various product channels

are determined. These experiments are expected to provide detailed dynamical data for testing theoretical potential surfaces and reaction trajectories.

234. Product Kinetic and Internal Energy Distributions via Velocity-Aligned Doppler Spectroscopy
C. Wittig **\$90,000**
Department of Chemistry

This research has focused on developing and applying an alternative method, velocity-aligned Doppler spectroscopy (VADS), to determine kinetic and internal energy distributions for photo-products and reaction products. The technique utilizes only a slight modification on conventional Doppler spectroscopy, yet the results can be quite revealing when compared with what one observes in a typical Doppler profile. Initial experiments have focused on the photodissociation of hydrides to produce hydrogen atoms. Examination of HBr (193 nm) and HI (193 and 248 nm) photodissociation has enabled spin-orbit populations and anisotropy parameters (β values) to be measured, and the results are interpretable within the context of spin-orbit coupling schemes. The 193 nm photodissociation of H₂S reveals the presence of significant vibrational excitation in the SH fragment. While in the photolysis of HBr, HI, or H₂S, most of the available energy is channeled into translational motion, NH₃ photolyzed at 193 nm produces relatively little translational excitation. The majority of the available energy appears as NH₂ vibrational and/or rotational energy. Efforts are under way to improve the resolution of the VADS method. Technological advances in the dye laser industry combined with sample cooling techniques can increase the energy resolution of the VADS technique markedly, and applying VADS to study molecules such as C₂H₂ looks promising. In addition, a variety of applications for the VADS method are being explored, including the study of photoinitiated cluster reactions. By using van der Waals forces to orient the reactants HBr and D₂ subsequent to HBr photodissociation, one can probe the H + D-D → H-D + D reaction in an environment where the initial conditions have been constrained.

SRI International
Menlo Park, California 94025

235. Flame Studies, Laser Diagnostics, and Chemical Kinetics
D.R. Crosley **\$130,000**
Molecular Physics Laboratory

This research project involves a combination of laser-induced fluorescence (LIF) and chemical kinetics measurements to investigate the chemistry 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 data base 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 the A³Π₁ excited state of the NH radical has been found to depend on rotational level, and that of the B²Π state of NS varies with vibrational level in different ways for different colliders. Quenching of the A²Σ⁺ of OH by H₂O in a low-pressure flame has been studied between 1200 and

2300 K, and a systematic investigation establishing quantitative determination of OH concentrations in the flame has been made. Experimental results together with transition state theory show that OH easily abstracts allylic hydrogens from butenes, in contrast to earlier studies on propene.

Stanford University
Stanford, California 94305

236. Spectroscopy and Kinetics of Combustion Gases at High Temperatures
R.K. Hanson, C.T. Bowman **\$125,000**
Department of Mechanical Engineering

This research focuses on two complementary activities: (1) development and application of 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 NH, NH₂, NCO, O, H, and OH radicals are of particular interest, and candidate source compounds for radical production are H₂O, NH₃, HN₃, HNCO, N₂O, NO, and H₂O₂. The primary excimer wavelength used for photolysis thus far has been 193 nm (argon fluoride), although other wavelengths are also of interest. Species to be investigated in the spectroscopic portion of the research include OH, NH, NH₂, and NCO.

University of Wisconsin
Madison, Wisconsin 53706

237. Unimolecular Reaction Dynamics and Vibrational Overtone Spectroscopy of Highly Vibrationally Excited Molecules
F.F. Crim **\$81,090**
Department of Chemistry

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 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.

Atomic Physics

Atlanta University
Atlanta, Georgia 30314

- 238. Theoretical Investigation of Electron-Ion Interaction**
A.Z. Msezane \$68,199
Department of Physics

The purpose of this project is to identify and calculate dominant physical mechanisms underlying the processes of electron impact excitation and ionization of ions and atoms of importance in astrophysical and laboratory fusion plasmas, using the close-coupling and R-matrix methods. Both total and differential cross sections are calculated and compared with measurements. In particular, detailed numerical studies are carried out to investigate (1) cascade contribution to the resonance transition in Ca II, important in solar and chromospheres, for comparison with absolute emission measurements; (2) coupling and inner-shell effects in low Z boronlike ions; and (3) the importance of correlations as a function of the nuclear charge through calculation of excitation energies and oscillator strengths for the inner-shell transition $2p^63s \rightarrow 2p^53s^2$, which leads to autoionization, in sodium isoelectronic sequence. Total and differential cross sections for electron impact excitation of Ca II and Cd II, important in the He-Cd II hollow-cathode laser, are compared with measurements from energy-loss spectrum and line emission data. Accurate configuration interaction wave functions of the targets are used to give the energy splittings between the ground state and the various excited states of interest very close to the observed values and the same values for the oscillator strengths in the length and velocity formulations.

California State University-Fullerton
Fullerton, California 92634

- 239. Correlated Processes in Atomic Collisions**
J.M. Feagin \$39,962
Department of Physics

Effort has been directed towards developing a simple molecular description of two-electron atoms in which the electrons move about the ion as a correlated pair. The three-body Coulomb potential would appear to provide the interelectronic axis with a rigidity, or false inertia, such that a strong correspondence with three-particle motion in molecular H_2^+ arises. Thus, a classification of electron-pair configurations in terms of the well-understood symmetries of diatomic molecules has been developed, and the striking similarities between He, H^- , and Ps^- observed in laboratory and numerical experiments have been obtained by a simple scaling of H_2^+ wave functions and energies. The molecular gerade/ungerade symmetry appears as a fundamental symmetry in atoms. Families of potential energy curves as a function of the interelectronic separation are being used to interpret collisionally induced electron-pair correlations in excitation (such as, $C^{9+} + He \rightarrow He^{**}$) and even in double capture reactions (such as, $O^{8+} + He \rightarrow O^{6+} + He^{2+}$). Propensity and selection rules for production of these configurations are being developed within the MO model. Related efforts include quantum diffusion computations to obtain precision energies and expectation values of dynamical variables, and a

calculation of the energy dependence of the threshold cross section for four-particle breakup of H_2 .

University of Colorado
Boulder, Colorado 80309-0440

- 240. Spectroscopic Diagnostics of Electron-Atom Collisions**
A.C. Gallagher \$91,445
Joint Institute for Laboratory Astrophysics

Fully differential cross sections for electron collisional excitation of sodium are being measured by a unique new method based on high-resolution laser spectroscopy. The angularly differential character of the excitation is detected through the Doppler-recoil spectrum of the excited atoms, and the angular momentum and spin dependence are detected as intensities of spectroscopically resolved Zeeman line components. Angularly total cross section measurements for the sodium resonance line have been made for electron energies near threshold. These results have already stimulated a reexamination of theories for this process. Angularly differential measurements for the same process are under way, and will be followed by measurements of higher state excitations in sodium.

- 241. Near-Resonant Absorption by Atoms in Intense Fluctuating Fields**
S.J. Smith \$95,000
Joint Institute for Laboratory Astrophysics

This research is an experimental investigation of the behavior of phased arrays of atoms coherently excited in a near-resonant very intense optical laser field, on which statistically well-characterized phase and frequency fluctuations have been imposed. The decorrelation of these phased dipole arrays is observed as the atomic phases evolve in time in the presence of perturbations. In this case, since the medium is quite diffuse, the important perturbations consist of the phase/frequency fluctuations of the optical field in which the atom is immersed. The parameters of the field fluctuations are determined by fully controlled experimental parameters. This provides a unique experimental environment in which to study the role of these controlled perturbations in the decorrelation process, in the absence of any other perturbations except spontaneous decay. Measurements on the Hanle effect in ytterbium (isotope 174) are complete and are being analyzed. The results show strong effects of the bandwidth and amplitude of the spectrum of fluctuations, and of the laser intensity, and clearly demonstrate the inadequacy of existing theoretical treatments. A new experimental study of phase noise decorrelation effects in the case of photon echoes in ytterbium is presently under development.

Cornell University
Ithaca, New York 14853

- 242. Experimental Study of Interactions of Highly Charged Ions with Atoms at keV Energies**
V.O. Kostroun \$270,100
Nuclear Science and Engineering Program

The goal of this project is to characterize experimentally the fundamental processes that occur in low-energy, very highly charged ion-atom(ion) interactions at temperatures and densities of matter typical of thermonuclear plasmas. The very highly

charged ions used in the experiments are furnished by the Cornell Electron Beam Ion Sources CEBIS I and CEBIS II, which produce such species by sequential electron impact ionization of ions trapped in an energetic, high-current-density electron beam. Ions available from these sources include all charge states of carbon, nitrogen, oxygen, and neon, including bare nuclei, argon charge states up to Ar^{16+} (helium-like), and xenon charge states up to Xe^{30+} . Both sources were designed and built at Cornell University. CEBIS II, a superconducting solenoid, cryogenic electron beam ion source, is the first successful source of this type to be constructed and operated in the U.S. During the past year, the first usable ion beams from these sources became available, and preliminary and exploratory electron and photon spectroscopy experiments involving argon ions with charge states $10+$ to $16+$ and kinetic energies around 300 eV/nucleon were initiated. Measured total electron and photon yields emitted in collisions of these ions with a titanium surface indicate that 10 to 30 photons and a comparable number of electrons per ion are emitted.

Georgia Institute of Technology Atlanta, Georgia 30332

243. *Statistical Fluctuations in Lasers* R. Roy \$67,903 School of Physics

The dynamics of spatial pattern formation for different transverse modes of a ring laser are currently being investigated. First passage time distributions for a laser with two or more transverse modes exhibit multiple peaks. Quantitative statistical measurements of the mode dynamics are obtained by analysis of these distributions. The effect of noise sources on the formation of the spatial patterns is also being investigated. The evolution of mode-locked pulses from a spontaneous emission background in synchronously pumped dye lasers is being studied by computer simulations. For the first time quantitative predictions of the pulse height statistics for these laser systems have been obtained and will be tested experimentally. The observation of stochastic resonance in a bistable ring laser in this laboratory has demonstrated for the first time that the addition of injected noise can lead to an improved signal-to-noise ratio of a periodically modulated system. Stochastic resonance is an essentially nonlinear phenomenon, requiring the presence of multiple stable states; the basic ingredients are generic enough such that the phenomenon is expected to occur in a wide variety of physical systems.

244. *Metastable Enhancement of C^+ and O^+ Capture Reactions* E.W. Thomas \$57,578 School of Physics

Metastable ions exhibit collisional charge-transfer cross sections in gases that are up to an order of magnitude greater than for the ground state. This observation is obviously related to the smaller energy defect for metastable collisions, but for complex species is not yet amenable to detailed theoretical treatment. This project studies charge transfer for 20 to 100 eV C^+ and O^+ ions in H, He, and H_2 , comparing ground and metastable excited-state cross sections. A low-energy (20 to 2,000 volt) accelerator has been constructed with a well-controlled electron impact source that produces beams of ground state C^+ and O^+ ions or mixed metastable and ground state species in

a determined ratio. Cross-section measurements in H_2 and He targets will begin shortly. Simultaneous studies examine how metastable species influence ion-induced sputtering and electron ejection from surfaces; both processes may be related to electron-transfer mechanisms. It has been shown that ejection of atoms from Si surface by O^+ impact is identical for ground and metastable species. This is not surprising since ejection will be primarily by physical sputtering. For ejection from carbon, findings suggest that metastable O^+ ejects carbon more efficiently than ground state O^+ . The enhanced ejection is through formation of CO, a volatile species, in the mechanism of chemical sputtering.

Harvard University Cambridge, Massachusetts 02138

245. *Theoretical Studies of Highly Ionized Species* A. Dalgarno \$134,000 Harvard-Smithsonian Center For Astrophysics

The influence of the plasma environment on the cross sections for transitions between the fine-structure levels of the $n = 2$ excited states of hydrogen-like ions induced by electron and proton impacts has been studied in a model that employs a screened Coulomb potential. The cross sections may be reduced substantially in magnitude. The stability of multiply charged molecular ions is under investigation and detailed predictions have been made of the energy level structure of OH^{2+} , OH^{3+} , and CH^{2+} . Radiative quenching of metastable helium in collisions with helium atoms has been treated. A theory of charge transfer in which explicit account is taken of the fine-structure levels has been applied to collisions of O^{3+} ions with hydrogen.

Jackson State University Jackson, Mississippi 39217

246. *Velocity Modulation Electronic Absorption Spectroscopy* B.C. Hale \$47,650 Department of Chemistry (24 mo.)

The chemistry of molecular ion reactions is important for many processes, such as plasma and combustion systems. In addition, many practical devices (e.g., lasers) depend on the existence of ions. However the amount of spectroscopic and dynamical information of ionic processes is very limited. The project objective is to develop and put into use a velocity-modulation electronic absorption spectrometer. We will study such ions as O_2^+ , CH^+ , and HCl^+ . We are also interested in quantitative measurements of spectral linewidths, lineshifts, and intensities. These measurements will allow us to study the dynamics of plasmas.

University of Kansas Lawrence, Kansas 66045

247. *Theoretical Studies of Many-Body Processes in Atomic and Molecular Physics* S.-I. Chu \$76,000 Department of Chemistry

The project objective is to develop new theoretical formalisms and practical computational methods for *ab initio* investigations of a number of atomic and molecular processes in intense laser

fields as well as the structure and dynamics of many-body resonances of current significance in science and technology. The projects being pursued currently are: (1) development of classical time-dependent self-consistent field approaches for the study of multiphoton excitation (MPE) and dissociation (MPD) of molecules in intense laser fields, (2) development of a most probable path approach (Floquet theory + artificial intelligence algorithms) techniques for probing MPE dynamics and quantum diffusion phenomena in Rydberg atoms, (3) development of a non-Hermitian Floquet matrix method for the treatment of intensity-dependent threshold shift and above-threshold multiphoton ionization (MPI) of complex atoms, and (4) development of Floquet-Liouville Supermatrix (FLSM) approaches for nonperturbative treatment of various time-dependent and intensity-dependent nonlinear optical processes.

**Kansas State University
Manhattan, Kansas 66506**

248. Atomic Physics of Strongly Correlated Systems
C.D. Lin **\$108,000**
Department of Physics

This project is directed toward the study of correlations and the scatterings of three charged particles of arbitrary masses. The Schroedinger equations for the three-body systems are expressed in terms of mass-weighted hyperspherical coordinates starting from the Jacobi coordinates of the system. By using mixed sets of Jacobi coordinates, it is shown that this method allows the solution not only of the bound states but also of the scattering problems. Currently the resonances of the three-body systems (such as, $e^+e^-e^-$, e^+p^+ , $d^+\mu^+$, $d^+\mu^+d^+$, and so forth) are being analyzed and classified. Two-electron processes in ion-atom collisions and the role of electron correlations in the resonant and nonresonant contribution of transfer excitation (TE) processes are also being studied. In TE processes a projectile electron is excited with a simultaneous capture of an electron from the target. This problem is solved by using a coupled channel formulation with full account of electron correlations in the two-electron wave functions. Results indicate the failure of the impulse approximation that is commonly used in the description of TE processes.

249. Atomic Physics with Highly Charged Ions
P. Richard **\$1,400,000**
Department of Physics, J.R. MacDonald Laboratory

Angular distributions of doubly and singly ionizing collisions of 3 to 9 MeV protons with helium, and cross sections for ionization, excitation, and transfer ionization of molecular deuterium by bare and hydrogen-like oxygen projectiles at energies between 7.5 and 30 MeV have been measured. At the Berkeley ECR source, the angular dependence of multiple electron capture in 90 keV Ne^{+7} collisions with neon has been measured. The cross sections for transfer ionization in $F^{+9} + He$ collisions have been determined for 9.5 to 38 MeV projectiles. Zero degree electron spectroscopy has been performed for $F^{+7} + He$ collisions. A 20-watt copper vapor laser and two dye laser systems have been installed and tested. An associated lithium vapor target cell and a zero degree electron spectrometer have been built to study laser-excited lithium-atom-ion collisions. A multidimensional coincidence experiment has been initiated in which outgoing electrons, recoiling target ions, and projectile

charge states and scattering angles are measured simultaneously. The cross sections for producing singly ionized molecular fragments have been successfully described by quasi-equilibrium theory, which divides the process into a sudden ionization followed by statistical fragmentation. The density matrix formulation has been adopted to study the orientation, alignment, and the dipole moment of the electronic charge cloud for excitation and charge-transfer processes in ion-atom collisions. Calculations of atomic parameters for dielectronic satellite lines of hydrogen-like ions ($Z = 18, 20, 26$, and 28) have been completed in the intermediate-coupling scheme with the inclusion of configuration interaction. Calculations of many-body effects in atomic scattering have been performed and have supported experimental observations of single and multiple ionization with photons, protons, antiprotons, electrons, and positrons.

**Louisiana State University
Baton Rouge, Louisiana 70803**

250. Electron Collisions with Positive Ions
R.J.W. Henry **\$68,800**
Department of Physics and Astronomy

The fundamental goal of this project is to delineate the important physical processes governing electron impact excitation processes for impurity ions in high-temperature plasmas of interest in thermonuclear reactors. The energy range considered is from the threshold to approximately four times the ionization energy. Calculations are based on a close-coupling expansion, which includes the important physical effects of electron exchange and resonances. A twelve-state close-coupling calculation, which includes excitation-autoionization and the effects of resonance excitation double autoionization (REDA) averaged over 2eV energy bins, has been performed for Fe^{+15} . The close-coupling results do not show a large enhancement of the cross section because of the REDA process, in agreement with recent measurements and in contrast to some predictions. Accurate electron-impact differential cross sections for various optically forbidden transitions in CuI, MgII, and ZnII were used to calculate apparent generalized oscillator strengths (GOS) in the electron impact energy range $15 < E < 100$ eV. Most curves of the GOS versus momentum transfer squared appear compatible with the Lassetre limit theorem.

**University of Louisville
Louisville, Kentucky 40292**

251. Spectroscopic Studies of Hydrogen Atom and Molecule Collisions
J. Kielkopf **\$73,500**
Department of Physics

Collisions involving the simplest neutral atomic and diatomic systems are studied using spectroscopic techniques. The work is designed to increase understanding of (1) the formation of atomic spectral lines as determined by radiative collisions and (2) the effects of collisions on shifts, widths, and intensities of unresolved components. While hydrogen offers a most tractable system from the point of view of theoretical modeling for the isolated atom or molecule, the collision processes are still quite complex and offer new unexplored phenomena because of the atomic degeneracy. A fast pulsed discharge in hydrogen and

hydrogen-rare gas mixtures is used to produce a strong time-dependent density of atomic hydrogen. These atoms interact with one another, with background molecular hydrogen, and with the rare gas buffer. A delay between the production of the hydrogen and its observation provides the control of density and other source conditions needed for studies of neutral collision processes. Measurements made with an excimer-pumped dual dye laser system, and with a five meter vacuum ultraviolet monochromator, will provide data on spectral line shapes, continua, and intensities.

**National Bureau of Standards
Boulder, Colorado 80303**

252. *Atomic and Molecular Collision Processes*
D.W. Norcross **\$80,000**
Quantum Physics Division

The focus of this project is computational studies of one of the most fundamental processes in laser and fusion plasmas: collisions of low-energy electrons with atoms and atomic ions. Recent progress includes state-of-the-art calculations for electron-impact excitation of lithium-like beryllium, confirming a large and disturbing discrepancy between measured and calculated results. Preliminary results have also been obtained for electron-impact excitation of sodium-like aluminum, a very similar species. These calculations are based on the highly sophisticated close-coupling approach. They employed both pseudostates to incorporate highly excited states and the continuum in the close-coupling expansion, and one-body and two-body terms in the potential to allow for polarization and correlation interactions between the outer electrons and the ionic core. For Al^{++} , for example, the latter is a 10% effect in cross sections for the resonant 3s-3p excitation. As an additional check on these calculations, binding energies and oscillator strengths for bound states of the compound system (e.g., Al^+) are also computed and compared with measurements and other calculations. In some cases these results provide data that are either new or more reliable than that previously available.

**National Bureau of Standards
Gaithersburg, Maryland 20899**

253. *Electron-Atom Collision Studies Using Optically State-Selected Beams*
R.J. Celotta, M.H. Kelley **\$78,980**
Radiation Physics Division

State selection in electron-atom collision studies greatly enhances the ability of experiments to provide critical comparisons with theory. When all quantum mechanical observables are resolved, discrepancies which are otherwise averaged out are often exposed. In the present work, scattering experiments are performed with spin-polarized electrons and optically state-selected atoms. Measurements have been performed on superelastic scattering of 2 eV electrons from optically pumped $Na(3P)$, and on elastic scattering of 54.4 eV electrons from spin-polarized sodium in the ground state. In the superelastic work, disagreements with well established theory are seen, and, because of the spin resolution of the experiment, the cause of these disagreements can be traced to either the singlet or the triplet channel. Elastic measurements show the interesting result that both spin-orbit and exchange effects must be treated

on an equal footing to achieve agreement with experiment, a surprising conclusion given the light target ($Z = 11$) and low-incident energy. Work to fill in the energy range between 2 eV and 54.4 eV is under way, with emphasis on critical analysis of theoretical methods to find regions where decisive measurements can be made. Future work will involve spin detection for the scattered electron to measure the relative phase between singlet and triplet scattering, and also investigations of other atomic species.

**University of Nebraska
Lincoln, Nebraska 68588-0111**

254. *Hyperspherical Coordinate Theory of Two-Electron Atomic Processes*
A.F. Starace **\$60,000**
Department of Physics and Astronomy

The main focus of this project is the theoretical study of correlated motion in three-particle systems interacting via the Coulomb interaction. The theoretical approaches are primarily based on the hyperspherical coordinate description of such systems. Applications are made to specific atomic collision processes where this approach can elucidate the underlying physical mechanisms. This study of electron detachment in H^- collisions with gas targets has shown that electron correlations are critical for interpreting observed electron spectra, the polarization of quench radiation, and relative populations of excitation channels. Definition of new types of excitation channels represents a major innovation of the hyperspherical method. An analysis of the anisotropy parameters for the photoionization of helium shows that these new excitation channels, which include electron correlations, are indeed populated at the photoionization thresholds. Other applications include the calculation of binding energies of loosely bound states of the helium trimer, the general theory of muon-atom interactions, and the alignment of collision excited atomic states.

**University of New Mexico
Albuquerque, New Mexico 87131**

255. *Relativistic Atomic Beam Spectroscopy*
H.C. Bryant **\$90,000**
Department of Physics and Astronomy

The structure of the H^- ion is being explored using laser probes and a beam with near luminal velocity. The photodetachment spectrum near the single electron threshold at 0.75 eV is studied under both σ and π polarized light in the presence of electrostatic fields ranging up to 60 kV/cm and in motional electric fields as high as 2 MV/cm. Using the same technique, cross sections for the production of high-lying doubly excited states in H^- , embedded in the 1P continuum, will be measured, and the double detachment cross section will be determined with a precision adequate to distinguish between the Wannier and Temkin theories. The yields of excited hydrogen states resulting from the passage of H^- at relativistic velocities through thin foils will be determined. The dependence of yield on foil thickness, material, and magnetic substrate will be observed. The kinematics of the interaction of a photon beam with a relativistic atomic beam will make possible the study of multiphoton processes in H^- as a function of wavelength and intensity, using a pulsed CO_2 laser.

**Pennsylvania State University
Lehman, Pennsylvania 18627**

- 256. *Electron Transfer, Ionization, and Excitation in Atomic Collisions***
T.G. Winter **\$29,507**
Department of Physics

Electron transfer, ionization, and excitation in ion-atom collisions are studied theoretically. Simple one- or at most two-electron systems are considered; accurate calculations can then be performed and the collisional mechanisms studied unambiguously. At the important range of energies (keV) being considered, coupled-state methods are the most appropriate. In the past year, using a triple-center, coupled-state approach, two collision processes have been studied in detail: ionization and electron transfer in collisions between alpha particles and H(1s) atoms as well as between protons and He⁺(1s) ions. In the case of alpha-particle-H collisions, individual-state processes and the dependence of electron transfer and elastic scattering on scattering angle have also been studied. These calculations have yielded accurate results for two prototype collisions over a wide range of energies and have placed limits on the range of validity of earlier molecular-state results. For both alpha-particle-H and p-He⁺ collisions, the triple-center approach has proven to be effective in describing ionization of electrons from the saddle point of the electronic potential between the projectile and target nuclei.

**University of Pittsburgh
Pittsburgh, Pennsylvania 15260**

- 257. *New Infrared Photon Absorption Processes***
J.E. Bayfield **\$120,000**
Department of Physics and Astronomy

This investigation determines how highly excited atoms lose their quantum structure and exhibit chaotic classical electron motion in the presence of intense optical fields. Theoretical predictions that this phenomenon (already observed in microwave fields) should scale to optical frequencies if the electron binding in the atom and the strength of the field are increased, will be examined. Hydrogen atoms with a principal quantum number equal to five will be exposed to midinfrared laser pulses of a few picoseconds duration and to intensities of 1 to 10 gigawatts per square centimeter. Under these conditions, the atoms are expected to undergo classically chaotic many photon absorption at rates larger than for resonant quantum multiphoton absorption. The transition probabilities to other bound states of the atom and for ionization of the atom will be measured. Probability distributions will be determined to discriminate between the classically chaotic and the quantum multiphoton absorption mechanisms.

**Purdue University
West Lafayette, Indiana 47907**

- 258. *Nonlinear Optical Interactions Involving the Real Gaussian Field***
D.S. Elliott **\$52,958**
School of Electrical Engineering

The goal of this experimental project is to determine the effect of laser bandwidth on nonlinear optical interactions. In particu-

lar, a laser field known as the Real Gaussian Field is being synthesized in which the amplitude of the field is a randomly fluctuating (Gaussian) process. Principal efforts thus far have been directed toward developing a technique for the random amplitude modulation of the output of a stabilized cw dye laser source. This requires an extremely high degree of compensation of several undesirable properties of electro-optic crystals. Upon completion of the development of this technique, this field will be applied to nonlinear optical processes such as two-photon absorption and intense field single-photon interactions. This experiment will provide a source of information for direct comparison with other theoretical works that have treated this effect. These results will aid the understanding of the effect of the bandwidth of broadband lasers that are routinely used for a variety of analytical, diagnostic, and spectroscopic applications.

**Rice University
Houston, Texas 77005**

- 259. *Theoretical Atomic and Molecular Physics***
N.F. Lane **\$109,780**
Department of Physics

Theoretical methods have been applied to calculate cross sections, rates, and other measurable parameters for a variety of atomic and molecular collision processes. Significant progress has been made in the areas of (1) alignment and orientation of excited orbital in collision of H + He; (2) quenching of Rydberg states of sodium in collision with helium; (3) state changing of Rydberg rubidium atom in collision with HF; (4) chemiionization of potassium by metastable helium; (5) chemiionization and ion pair production in collision of lithium with metastable helium; (6) charge transfer in collision of highly stripped ions with helium and H₂ at KeV energies; (7) charge transfer in slow collision of He⁺ with H₂; (8) radiative and nonradiative charge transfer in collision of He⁺ with H; and (9) elastic electron scattering from large molecules. Research is continuing on these and other similar processes and on the development of new theoretical methods.

**University of Rochester
Rochester, New York 14627**

- 260. *Nonlinear Optics with Broad-Band Lasers***
M.G. Raymer **\$98,000**
Institute of Optics

Experimental and supportive theoretical work is being conducted to reveal the statistical properties of broad-band laser radiation and the influence such properties have in certain nonlinear optical processes. Both continuous (cw) and pulsed dye lasers are being studied. A new method has been discovered to produce intense, broadband (5 GHz) light pulses with pure phase fluctuations and smooth amplitude. In addition, the mode intensity fluctuations in multimode, cw dye lasers are being measured directly for several different laser cavity configurations. Such fluctuations are important because they limit the sensitivity of intracavity laser spectroscopy, an extremely sensitive technique for detecting low-concentration molecular species. The fluctuations have been found to be deterministically chaotic, that is, they appear random and are not periodic; nevertheless, they arise from strictly deterministic motion. In

this case it was found that four-wave mixing in the laser gain medium is responsible for this behavior. Future study will investigate whether quantum mechanical noise can also contribute to the fluctuations in some situations.

St. John Fisher College
Rochester, New York 14618

- 261. Multilevel Relaxation Phenomena and Population Trappings**
F.T. Hioe **\$72,000**
Department of Physics

This theoretical research deals with various aspects of a multilevel quantum system interacting with an intense laser field. Analytic solutions have been derived that give the precise conditions for completely inverting the atomic population and that clearly identify the single most important parameter on which the final outcome would depend. Moreover, the analytic solution predicts that under many experimental situations, various combinations of the level population, besides the total sum, remain constant in time. The invariants are related to specific types of SU(N) dynamic symmetry. It is planned to make use of these analytic solutions to study (1) the conditions for multiple-pulse propagation through the atomic media without attenuation, and (2) the circumstances that would give rise to a possible detection of Berry phase.

University of Tennessee
Knoxville, Tennessee 37996-1200

- 262. Production and Destruction of Metastable Negative Ions**
D.J. Pegg **\$46,000**
Department of Physics and Astronomy

The destruction of negative ions by photoabsorption is being studied. The source of the negative ions is a tenuous, fast-moving beam produced by charge changing a beam of positive ions in an alkali vapor cell. Photon-negative ion collisions are investigated in the interaction region between perpendicularly crossed ion and laser beams. Photoelectrons detached from the negative ions into the forward direction are collected, energy analyzed, and detected by an electrostatic electron spectrometer. The resulting photoelectron spectra are used to determine the structure of the negative ions. Angular distributions of the ejected photoelectrons can also be mapped out by rotating the electric field vector of the linearly polarized laser beam. During the past year the structure of Ca^- has been determined for the first time. This ion is, contrary to earlier expectations, stably bound in the $(4s^2 4p)^2 P$ state. The electron affinity of calcium has been measured to be 43 MeV.

University of Texas
Austin, Texas 78712

- 263. Kinetic Studies Following State-Selective Laser Excitation**
J.W. Keto **\$91,000**
Department of Physics

State-to-state rates for reactive energy transfer from excited rare gas atoms to halogen molecules are measured. The atoms are excited in two-photon transitions using ultraviolet lasers.

Accurate ($\pm 2\%$) measurements of the reaction rate from $\text{Xe}^* 6p$ to Cl_2 in both xenon buffer gases have just been finished. Very large bimolecular rates have been measured and compared with a multichannel, curve-crossing theory. Good agreement is found between theory and experiment. A large termolecular reaction rate has also been measured. These measurements are being extended to argon buffer gases with both Cl_2 and HCl reactants. These reaction rates are required for modeling of the XeCl excimer laser. In order to make these measurements accurate values for quench rates of excited xenon atoms in argon buffer gases have first been measured. The $\text{Xe}^+ - \text{Cl}_2^-$ reaction complex formed by exciting collision pairs in a gas cell or bound pairs in a supersonic beam is under study. In preliminary experiments, dramatic variations have been found in the energy disposal in the reaction products as a function of the wavelength of light used to excite the pairs onto the ionic potential surface.

Texas A and M University
College Station, Texas 77843

- 264. Excitation of Atoms and Molecules in Collisions with Fast, Highly Charged Ions**
R.L. Watson **\$80,992**
Cyclotron Institute

Beams of fast (MeV/nucleon), highly charged ions are used to create multiple inner- and outer-shell vacancies in gaseous and solid targets. A major topic of investigation is molecular fragmentation resulting from the removal of 1 to 10 electrons from the valence orbitals of simple gas molecules. Molecular ions with lifetimes greater than 0.1 microseconds and fragments from the breakup of highly excited molecules are identified by time-of-flight mass spectrometry. In other experiments, the spectra of x rays emitted as a result of the radiative decay of inner-shell vacancies are measured in high resolution using a variety of spectrometer systems. The x-ray spectra provide information concerning the energies, intensities, and identities of the excited states produced in the collision, and reveal evidence of fast (femtosecond) relaxation processes. A recent investigation of double K-vacancy states in oxygen has shown that correlated two-electron transfer from neighboring atoms plays an important role in the de-excitation process for certain compounds.

University of Toledo
Toledo, Ohio 43606

- 265. Semiempirical Studies of Atomic Structure**
L.J. Curtis **\$47,000**
Department of Physics and Astronomy

The goal of this project is to build up a precise, comprehensive, and reliable base of atomic structure data in highly ionized many-electron systems through the combined use of sensitive semiempirical data systematizations, selected precision experimental measurements, and specialized theoretical computations. The atomic properties studied involve (1) primary data, such as wavelengths, frequency intervals, transition probabilities, lifetimes, and so forth, and (2) derived structural data, such as energy levels, ionization limits, polarizabilities, excitation functions, and so forth. Measurements are made primarily through the use of fast ion beam excitation methods, which are combined with available data from laser- and tokamak-

produced plasmas, astrophysical sources, and conventional light sources. The experimental studies are strengthened through large-scale *ab initio* calculations using the MFE Cray X-MP computer. Large blocks of data are systematized and parameterized along isoelectronic, homologous, isoionic, Rydberg, and yrast series. Recent studies have emphasized forbidden transitions in heavy and highly ionized systems, radiative transitions in multiply excited few-electron systems, the spectroscopy of highly ionized members of the neon and sodium isoelectronic sequences, and transition probabilities in systems heavily influenced by cascade repopulation.

Vanderbilt University
Nashville, Tennessee 37235

266. Theoretical Studies of Atomic Transitions
C.F. Fischer **\$110,000**
Department of Computer Science

Atomic structure calculations are being performed to predict properties such as energy levels, binding energies, and lifetimes of excited states. Of particular interest recently has been the prediction of binding energies of neutral atoms and negative ions such as Ca^- and Sr^- , previously classified as ions with no stable bound states. To assist in the identification of observed data, autoionization calculations have been performed for some high-spin states of core excited Na^- . Calculations were based on the MCHF methods of including correlation effects. In the case of the negative ions, the energy levels were corrected for relativistic shifts effects. In the autoionization calculations, the wave function was corrected for relativistic effects through the Breit-Pauli approximation. The MCHF codes presently are being modified for more convenient use on the CRAY for large problems. They also are being extended to photoionization studies in the presence of resonances as in magnesium.

University of Virginia
Charlottesville, Virginia 22901

267. Studies of Autoionizing States Relevant to Dielectronic Recombination
T.F. Gallagher **\$98,859**
Department of Physics

Autoionizing states play a key role in the process of dielectronic recombination, an important energy loss process in tokamak plasmas. Using laser spectroscopy we are investigating the basic atomic properties of autoionizing states to provide the microscopic understanding of dielectronic recombination necessary to understand macroscopic plasmas. We are presently finishing measurements of the autoionization rates of high ℓ Ba $6p\ell$ autoionizing states. The autoionization rates of high ℓ states are particularly important because of their high statistical weight. Since the high ℓ states are optically inaccessible from the ground state, we use a Stark switching technique to populate the bound $6sn\ell$ states. The autoionization linewidths of the $6p\ell$ states span a range of four orders of magnitude for $0 \leq \ell \leq n-1$, requiring a saturation technique for the measurements of the narrowest states. The resulting rates are in good agreement with relatively simple calculations, which indicates that dielectronic recombination rates can be calculated with some confidence. We have begun the measurement of autoionization rates in time varying fields, to approximate the electric microfields from the

ions in a plasma. To date all theoretical treatments of this problem have assumed that the fields vary on a time scale slow compared to autoionization rates. This, however, is rarely the case for high ℓ states that have the largest statistical weight. These measurements will either substantiate or contradict the present theories.

Western Michigan University
Kalamazoo, Michigan 49008-5151

268. Correlated Charge-Changing Ion-Atom Collisions
E.M. Bernstein, J.A. Tanis **\$74,000**
Department of Physics

Experimental studies of fundamental atomic interactions, with a major emphasis on two-electron interactions, are conducted for collisions of few-electron ions with neutral gas targets. In the case of two-electron interactions, the electrons may act independently, or there may exist correlation effects that need to be considered (this latter aspect being a subject of considerable current interest). The use of few-electron ions permits the study of both one- and two-electron processes under conditions where screening effects can be minimized or eliminated. The measurements generally involve heavy ions ($8 \leq Z \leq 92$) in high charge states ($q \geq Z/2$) with energies ranging for 0.1 to 10 MeV/u. Individual processes of excitation, ionization, charge transfer, and combinations of these are investigated using coincidence techniques to isolate and identify the interaction mechanisms of interest. Specific studies include resonant and nonresonant transfer and excitation, combined projectile excitation and ionization, target ionization accompanied by projectile electron capture or loss, and correlated double capture. Measurements are conducted using accelerators at the Lawrence Berkeley Laboratory, Brookhaven National Laboratory, Argonne National Laboratory, and Western Michigan University.

The College of William and Mary
Williamsburg, Virginia 23185

269. Collisional Detachment of Negative Ions
R.L. Champion, **\$92,000**
L.D. Doverspike
Department of Physics

Experimental studies are focused on investigations of negative ion-atom (or molecule) collisions for collision energies below 500 electron volts. The experiments involve measurements of absolute total and differential cross sections for a number of exit channels as well as an investigation of anion formation on alkali surfaces. The goal of the experiments is to develop an understanding of the various reaction mechanisms important in processes that involve negative ions. Systems currently being studied include the negative ions of hydrogen, deuterium, SF_6 , oxygen, and certain alkali metals in collisions with a variety of atomic and molecular targets. An atomic hydrogen source under development will extend the measurements to include atomic hydrogen (or deuterium) targets. Mechanisms under investigation include collisional detachment, charge transfer and dissociative charge transfer, and associative detachment.

Chemical Energy

Brigham Young University Provo, Utah 84602

270. *Effects of Dispersion and Support on Adsorption, Catalytic, and Electronic Properties of Cobalt/Alumina CO Hydrogenation Catalysts*
C.H. Bartholomew **\$109,000**
Department of Chemical Engineering (16 mo.)

An investigation of the effects of surface structure, dispersion, and support on the adsorption, catalytic, and electronic properties of cobalt/alumina is in progress. The project objectives are (1) to determine the effects of surface structure and metal dispersion on the adsorption and catalytic properties of cobalt and (2) to determine the effects of decorating support species on metal crystallites and of direct electronic interactions between metal clusters and support, on the adsorption, catalytic, and electronic properties of cobalt supported on alumina. Work has been divided into three areas of study: (1) study of the effects of surface structure and support decoration on the adsorption and catalytic properties of cobalt monolayers deposited on W(100) and W(110), using TPD, LEED, and AES spectroscopies, and *in situ* CO hydrogenation reaction measurements; (2) study of the effects of dispersion and support decoration on the CO adsorption/desorption and catalytic properties of well-dispersed cobalt/alumina, using TPD and IR spectroscopies and lab reactor measurements; and (3) Mossbauer study of the effects of metal-support interactions and decoration on the electronic properties of well-dispersed cobalt/alumina and iron/alumina.

University of California Irvine, California 92717

271. *Synthesis and Chemistry of Yttrium and Lanthanide Metal Complexes*
W.J. Evans **\$87,000**
Department of Chemistry

Investigations are in progress for using the special chemical and catalytic properties of yttrium and the lanthanide metals, a group of elements that has a unique combination of steric and electronic features and that is abundant in the U.S. Studies of metal-carbon and metal-hydrogen bond reactivity in cyclopentadienyl complexes of these metals have shown that their special chemistry can be precisely controlled by varying the amount of steric saturation around the metal. This provides a basis to accomplish highly selective transformations. Complexes that contain coligands more robust than cyclopentadienyl ligands are now being studied in order to perform reactions with a wide variety of substrates and reaction conditions. A series of alkoxide and alkoxide oxide complexes based on trimetallic subunits that are ideal for this were discovered and structurally characterized. Since the environment around the metal in these complexes resembles that in metal oxides, these compounds also may be good models for metal oxide catalysts and catalyst supports. The effect of the metal oxide environment on metal-carbon and metal-hydrogen bond reactivity will be compared to previous data and used to try to develop highly selective catalytic reaction cycles.

University of California Santa Barbara, California 93106

272. *Homogeneous Catalysis of the Water Gas Shift Reaction*
P.C. Ford **\$110,000**
Department of Chemistry

This research project involves continuing investigations of fundamental reactions relevant to the development of new homogeneous catalysts for the activation of carbon monoxide. These include mechanistic studies of the water gas shift and related CO reactions as catalyzed by metal complexes dissolved in homogeneous solution or immobilized by coordination to polymers functionalized with different chelating amine groups. Also under quantitative investigation are mechanisms for formation and subsequent reactions of nucleophile-carbonyl adducts of various mono- and polynuclear metal complexes, for ligand transformations on metal clusters related to the catalytic use of C_1 fragments and for the formation and reactions of metal hydride ions prepared by the protonation of low-valent metal complexes. The goals are to delineate the mechanistic principles that dictate effective catalysis of C_1 compounds, thus to establish and extend chemical guidelines for molecular engineering of new catalysts for the use of coal and biomass as feedstocks for chemical and fuel production.

California Institute of Technology Pasadena, California 91125

273. *Fundamental Studies of Olefin and Acetylene Insertion Reactions*
J.E. Bercaw **\$100,000**
Department of Chemistry

This project studies the scope, mechanism, and thermodynamics of olefin and alkyne insertion into metal-hydrogen and metal-carbon bonds. Studies included the mechanisms for the reversible insertion of coordinated olefins into Nb-H and Ta-H bonds for the system $(\eta^5-C_5R_5)_2M(CH_2=CHR')H$ ($M = Nb, Ta$; $R = H, CH_3$; $R' = H, CH_3, C_6H_5, C_6H_4X$ [$X = OCH_3, NMe_2, CF_3$]). A consistent picture of the mechanism, including factors influencing ground and transition state energies, has emerged. For the well-behaved permethyltantalocene system, the relative propensities for α vs. β H elimination have been established and the mechanism of alkyl α migration to methylene ligands has been investigated. Recently, reversible olefin insertion/ β H and β alkyl elimination for $(\eta^5-C_5Me_5)_2Sc-R$ ($R = H, alkyl, and so forth$) were explored. Scandium systems investigations have discovered: (1) clean polymerization of ethylene to polyethylene with specified polydispersities, using well-defined (one-component) scandocene alkyl catalysts; (2) catalytic dimerization of α olefins to the head-to-tail, *gem*-disubstituted olefin with remarkable selectivities (>99% for >50 turnovers); (3) a related catalytic intramolecular cyclization of α, ω diolefins selectively to *exo*-methylene cycloalkanes; and (4) catalytic, reversible branching of 1,4-pentadienes to substituted 1,3-dienes. These reactions proceed by olefin insertion into Sc-H bonds/ β H elimination and olefin insertion into Sc-alkyl bonds/ β alkyl elimination sequences, the latter of which are facile for these highly Lewis acidic scandium complexes. Results have provided an understanding of some fundamental steps in olefin metathesis, dimerization, polymer-

ization, hydroformylation and hydrogenation, branching, and isomerization reactions.

274. Catalytic Assembly of Hydrocarbons from Carbon Monoxide
R.H. Grubbs **\$120,000**
Department of Chemistry

Models for the key steps in the assembly of hydrocarbons on metal centers have been developed. The most important of these are complexes that contain CH_2 bridge between a late and early transition metal. The reactions of these complexes with carbon monoxide produces bridging ketene complexes of the type studied in our labs earlier. The reactions of the following classes of compounds with CO , H_2 , and PR_3 have been studied. $[\text{Cp}_2\text{Ti}(\text{X})\text{CH}_2\text{ML}_n]$ where $\text{X} = \text{Cl, OR, SR, CH}_3, \text{Ph}$ and $\text{M} = \text{Rh, Pd, Pt, Ir, Zr, Ti}$ By attaching an alkyl ligand to the late transition metal, a variety of C-C coupling reactions can be studied and the relative reactivity of terminal and bridging carbon species can be examined. The multistep reduction of CO on a metal center has resulted in the synthesis of a variety of metal aldehyde and ketone complexes. These can be released to yield alcohols. These same complexes can be used to prepare the second example of a bridging trigonal bipyrimidal complex. This confirms the original structure and suggests that these species may be more common than normal.

University of Chicago
Chicago, Illinois 60637

275. Selective Chemical Methods for the Study of Coal Structures
L.M. Stock **\$70,000**
Department of Chemistry

New chemical methods for the investigation of the constitution of coal are being studied. In recent work, ruthenium (VII) has been developed as a selective oxidation reagent for the investigation of this problem and has been used to study an array of fossil materials. The scope of the reaction has been defined by the investigation of molecules thought to be representative of the constituents present in coal. The products of the oxidation of seven different coals have been defined and the products of three pure maceral groups have been characterized. Quantitative methods based on isotopic dilution techniques have been worked out and applied successfully for the determination of prominent structural features. This information is being used to generate the structural information about the coals and the macerals. The oxidation reactions of certain coals provide linear alkane carboxylic acids. These compounds may be produced by the ruthenium (VIII) oxidation of arylalkanes ($\text{ArR} \rightarrow \text{RCO}_2\text{H}$). This feature prompted an examination of the character of the linear polymethylene fragments in the coals. Several different tactics have been used to determine the relative abundances of alkanes and arylalkanes in several coals. In brief, most alkanes in most coals appear to be physically entrapped rather than covalently bonded. However, good evidence has also been obtained to support the view that C_{15} to C_{18} alkanes are physically entrapped whereas C_{21} to C_{25} alkanes may be covalently bonded. This finding may be readily rationalized on the basis of the idea that the lower molecular weight materials arise from microbial sources whereas the higher molecular weight materials arise from plant sources.

University of Colorado
Boulder, Colorado 80309

276. Studies of Hydrogen-Hydrogen and Carbon-Heteroatom Bond Cleavage Reactions
M.R. DuBois **\$60,000**
Department of Chemistry and Biochemistry

The objective of the project is to characterize hydrogenolysis reactions of dinuclear molybdenum complexes with bridging thiolate and sulfide ligands. Such reactions provide potential homogeneous models for the chemistry of the hydrodesulfurization catalysts. Certain cationic complexes of the type $[(\text{CpMo})_2(\text{S}_2\text{CH}_2)(\mu\text{-S})(\mu\text{-SR})]^+$ have been found to react with hydrogen to form RH , H^+ , and $(\text{CpMo}\mu\text{-S})_2\text{S}_2\text{CH}_2$. This reactivity shows a significant dependence on the nature of the thiolate substituent R. Recent studies have focused on the isomeric derivatives with vinylthiolate and allenylthiolate ligands $\text{R} = \text{C}(\text{Me})=\text{CHMe}$ and $\text{R} = \text{CH}_2\text{CH}=\text{C}(\text{H})\text{Me}$, respectively. Both isomers reacted with hydrogen to form 2-butene and at higher temperatures, 2-bromobutane. Proposed intermediates in the hydrogenolysis reactions have been synthesized and characterized. The position of the double bond in the thiolate ligand alters some aspects of chemical reactivity. For example, reaction of the vinyl thiolate derivative with basic nucleophiles led to a deprotonation reaction, while the allenylthiolate complex underwent nucleophilic attack at the bridging sulfide ligand. The difference in reactivity has been attributed to different isomerization pathways in solution which permit different resonance forms for the two isomers. Studies of the hydrogenolysis reactions of neutral derivatives of the type $(\text{CpMo})_2(\text{S}_2\text{CH}_2)(\mu\text{-SCH}_3)(\mu\text{-SR})$ have also been initiated. Preliminary studies suggest that the reaction with hydrogen to form RH and $(\text{CpMo})_2\text{S}_2\text{CH}_2(\mu\text{-SCH}_3)(\mu\text{-SH})$ is an acid-catalyzed process.

277. Chemisorption and Reaction Studies on Well-Characterized Bimetallic and Alloy Surfaces
B.E. Koel **\$71,665**
CIRES

This project explores the chemisorption and reactions of hydrocarbons on well-characterized, single-crystal bimetallic surfaces in order to understand the role of electronic and geometric effects in modifying the chemistry of these surfaces. Recent work has included studies of several important systems: (1) $\text{C}_2\text{H}_4\text{-K-Pt}(111)$; (2) $\text{C}_2\text{H}_4\text{-Bi-Pt}(111)$; (3) $\text{C}_2\text{H}_4\text{-Sn-Pt}(111)$; and (4) C_2H_4 and $\text{C}_2\text{H}_2\text{-C-Ni}(100)$, and $\text{O-Pt}(111)$. Potassium coadsorption causes the formation of a new, weakly bound, π -bonded state of C_2H_4 . At high potassium coverages, the mechanism for C_2H_4 decomposition passes through a stable CHCH_3 species. Bismuth and tin coadsorption acts to block platinum sites for C_2H_4 adsorption and decomposition, but does not affect the C_2H_4 binding energy. Work is in progress to model these results in order to determine surface ensemble requirements for ethylene reactions on platinum. Studies have been initiated on the reactions of C_2H_4 and C_2H_2 on $\text{Ni}(100)$ with the aim of explaining the structure sensitivity of this surface relative to $\text{Ni}(111)$ on the decomposition mechanisms. Work related to studies of the chemical modification of surface properties has also been done on the reaction kinetics of high coverages of atomic oxygen, $\theta_0 \leq 0.75 \text{ ML}$, on $\text{Pt}(111)$.

Colorado State University
Fort Collins, Colorado 80523

- 278. Chemically Modified Electrodes and Related Solution Chemistry**
C.M. Elliott **\$85,000**
Department of Chemistry

The primary goal of this research is the development of polymer coated electrodes containing electroactive materials which alter the chemical and/or physical properties of the electrode-solution interface in useful ways. Several such electrodes have been prepared. The fundamental processes of electron and ion transport in such modifying polymers are being studied. A new type of electronically conducting "organic" polymer has been developed and is being studied. There are two aspects to studying chemically modified electrodes: (1) developing schemes for incorporating electroactive systems of interest into polymers; and (2) developing and studying molecules (e.g., catalysts) that are of potential interest for incorporation into polymer films. Different synthetic procedures appropriate for each material under study are investigated in order to chemically incorporate the molecules of interest into polymers. For example, a number of novel metalloporphyrins have been prepared, and their redox chemistry is under investigation both in solution and polymer-bound. Polymer films formed from these porphyrins on electrode surfaces catalyze the oxidation of certain olefins in solution. 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.

- 279. Diosmacycloalkanes as Models for the Formation of Hydrocarbons from Surface Methylene**
J.R. Norton **\$80,000**
Department of Chemistry

This project has developed several efficient general syntheses of diosmacycloalkanes. These syntheses were used to prepare compounds that may serve as models for hydrocarbons and hydrocarbon fragments adsorbed to metal surfaces. The structures and the reactivity of several of these compounds were explored. It was shown that, in contrast to accepted theory, ethylene exchanges in and out of diosmacyclobutane occurred with retention of stereochemistry at carbon. Aromatic- and alkyl-substituted olefin adducts are in preparation (1) to explore any alternative olefin elimination pathways and (2) to identify these compounds as models for metal surface-bound alkenes. Several larger ring diosmacycloalkanes were prepared that serve as models for methylene aggregation on the surface of Fischer-Tropsch catalysts. The properties of these dinuclear-dialkyl compounds will be compared to their mononuclear analogs to determine which (if any) steps in typical catalytic sequences require the presence of polynuclear systems.

- 280. Heterobimetallic Complexes for Carbon Monoxide Reduction**
J.K. Stille **\$86,000**
Department of Chemistry

The objective of this research is to synthesize certain homogeneous heterobimetallic catalysts, containing both an early and a late transition metal, that will provide information on the bonding and mechanisms involved in carbon monoxide reduction. Ultimately, this information should be useful in designing a catalyst that will reduce carbon monoxide selectively under mild reaction conditions. Heterobimetallic catalyst synthesis is emphasized because there are a number of examples of heterogeneous catalysts that are mixed metal oxides or mixed alloy catalysts that reduce carbon monoxide under relatively mild conditions more selectively than a catalyst composed of only one metal. Complexes containing combinations of early (e.g., niobium and molybdenum) and late (e.g., iron, cobalt, and rhodium) transition metals that could be expected to activate carbon monoxide most effectively are primary targets. The late transition metals were selected because they are the most efficient in heterogeneous catalysts used in Fischer-Tropsch and other carbon monoxide reductions. By the synthesis of such heterobimetallic catalysts and the observation of the interaction of the ligands on the two metal centers, the answer to some fundamental mechanistic questions surrounding the individual steps in the reduction of carbon monoxide should be available.

University of Connecticut
Storrs, Connecticut 06268

- 281. Structure Sensitivity of Iron and Cobalt Zeolite Catalysts**
S.L. Suib **\$65,000**
Department of Chemistry

This research project concerns the structure sensitivity of cyclopropane and ethane reactions over cobalt and iron zeolite catalysts. Highly dispersed cobalt and iron catalysts that have metal particle sizes less than 5 angstroms have been prepared by microwave discharge processes. Larger size metal particles of 10 and 25 angstrom particle sizes have been prepared by thermal methods. Ring opening, hydrogenation, hydrogenolysis, and oligomerization reactions of cyclopropane all occur over variable particle size metal zeolite catalysts, and product selectivity can be controlled by varying the size and shape of the metal particles. Ring opening reactions predominate over catalysts with small metal particle size while hydrogenation and hydrogenolysis reactions occur over catalysts with larger metal particle size. All catalysts have been characterized by a variety of spectroscopic methods including ferromagnetic resonance, Mossbauer, transmission electron microscopy, Rutherford backscattering, and spin echo nuclear magnetic resonance (NMR) methods. Spin echo NMR data allow the determination of the structure and relative particle size of cobalt and the occurrence of alloy formation between iron and cobalt. Selective hydrogen deuterium exchange catalysts of sonicated Raney nickel and doped Raney nickel have also been studied. Ultrasonic cavitation cleans the surface of the Raney nickel, leading to crack propagation of the catalyst and an increase in selectivity and activity. The surfaces of all of both catalytic systems have been studied with x-ray photoelectron spectroscopy, Rutherford backscattering, and secondary ion mass spectrometry in

order to determine oxidation states, surface vs. bulk concentrations, and depth profile information.

University of Delaware
Newark, Delaware 19716

282. *Selectivity of the Reactions of Oxygenates on Transition Metal Surfaces*
M.A. Barteau \$75,000
Center for Catalytic Science and Technology

This research focuses on the adsorption and decomposition of alcohols, aldehydes, and carboxylic acids on transition metal surfaces, with emphasis on determining the influence of surface modifiers and surface structure on the interactions of oxygenates with rhodium and palladium surfaces. Oxygen plays no fewer than five roles in altering the selectivity of alcohol decomposition on Pd (111). The most important of these roles is the alteration of the binding of aldehydes to the surface. Aldehyde species in the η^1 configuration (i.e., attached to the surface via their carbonyl oxygen) desorb on the oxygen-dosed surface, whereas those adsorbed in an η^2 configuration (attached via both the carbonyl and oxygen atoms) decompose on the clean surface. The roles of other inorganic promoters on the adsorption and reaction of the intermediates involved in oxygenate synthesis, utilizing TPD, HREELS, and XPS as the primary investigative tools, are being explored. These studies are aimed at explaining the importance of metal and promoter characteristics in producing selective oxygenates synthesis, thus leading to the identification and optimization of metal catalysts for this purpose.

283. *Characterization of Metal-Support Bonds in Supported Metal Catalysts*
B.C. Gates \$106,000
Department of Chemical Engineering (15 mo.)

This research investigates 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 reactions of precursor metal carbonyls and metal allyls with the support surfaces, and characterized by EXAFS used in combination with temperature-programmed decomposition and infrared and NMR spectroscopies. Results are leading to elucidation of the metal-oxygen coordination at the surfaces and the exact metal-support bond distances. These structurally well-defined surface complexes are being reduced gently to convert the surface species into metal aggregates and ultimately into larger crystallites, with the process being followed by EXAFS and complementary techniques. Results are beginning to provide structural characterizations of a continuum of structures ranging from "molecular" precursors to conventional supported metals, with the first results having been obtained for osmium on Al₂O₃. These results are providing a foundation in molecular chemistry for understanding metal-support interactions in the broad class of oxide-supported metals.

Harvard University
Cambridge, Massachusetts 02138

284. *Model Studies of Hydrodesulfurization and Hydrodenitrogenation on Molybdenum Surfaces*
C.M. Friend \$102,355
Department of Chemistry (15 mo.)

Desulfurization reactions of benzenethiol and the saturated C₂ through C₅ cyclic sulfides and primary thiols have been investigated. Current focus is on the oxygen and nitrogen analogs of these molecules. A combination of chemical and spectroscopic methods are used to establish general principles governing structure and reactivity: temperature programmed reaction, x-ray photoelectron, high-resolution electron energy loss, Auger electron, and near edge x-ray absorption fine structure (NEXAFS) spectroscopies. A general mechanism for the reaction of cyclic sulfides on Mo(110) has been formulated. Four channels compete in the reaction of cyclic sulfides: (1) irreversible, nonselective decomposition, (2) formation of a thiolate intermediate that produces linear hydrocarbons, (3) intramolecular hydrocarbon elimination, and (4) molecular desorption. The selectivity of the cyclic sulfide reactions is controlled by ring size and strain. Thiols selectively form a thiolate intermediate that eliminates hydrocarbons through competing C-S bond hydrogenolysis and β -dehydrogenation. The kinetics for hydrocarbon formation depend strongly on the coverages of sulfur, carbon, molecular fragments, and hydrogen on the surface.

University of Illinois
Chicago, Illinois 60680

285. *In Situ Ultraviolet Diffuse Reflectance Studies of Heterogeneous Catalysis*
R.D. Gonzalez \$59,126
Department of Chemical Engineering

The effect of catalyst pretreatment on the surface composition of supported bimetallic clusters is currently under study using the following techniques: (1) *in situ* diffuse ultraviolet spectroscopy, (2) differential scanning calorimetry, and (3) electron microscopy. *In situ* diffuse ultraviolet reflectance spectroscopy is being used to probe the nature of the interactions between the metal precursors and the support. Current interest is on structural differences between catalysts prepared by impregnation and those prepared by ion exchange. Quantitative differential scanning calorimetry is being used to measure heats of reduction during the preparation of supported Pt-Ru bimetallic cluster catalysts. The reductive sequence is of current interest. Scanning transmission electron microscopy (STEM) is being used to measure individual particle compositions using (1) an imaging defocusing technique and (2) electron diffuse angle x-ray scattering (EDAX). For a series of supported Pt-Ru bimetallic cluster catalysts, the smaller bimetallic particles are alloyed. Larger ruthenium particles in addition to platinum particles are also present. True bimetallic clusters are favored for Pt-Ru compositions that are close to 50%.

Indiana University
Bloomington, Indiana 47405

- 286. Model Cu-ZnO Catalysts for Methanol Synthesis: The Role of Surface Structure**
C.T. Campbell **\$72,000**
Department of Chemistry

The catalytic conversion of synthesis gas to methanol promises to play a vital role in our nation's energy future. Preferred catalysts are now based on Cu-ZnO compositions, which are considerably more active than the separate components. The project objective is to develop a microscopic understanding of the role played by surface structure and composition in determining the activity and selectivity of Cu-ZnO catalysts for methanol synthesis ($\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$). This is achieved by correlating the kinetics of the overall catalytic reaction and its elementary steps with the detailed surface structure and chemical composition of model catalysts which are designed for maximum surface control. These model catalysts are prepared and characterized using the state-of-the-art techniques of surface science. In this way, the nature of the active site on Cu/ZnO catalysts is being addressed. Model Cu/ZnO catalysts based on Cu and ZnO have been structurally and kinetically characterized. In addition, the electronic interactions between Cu and ZnO in these catalysts have been addressed using a combination of electron spectroscopies and semi-empirical quantum chemical methods (INDO). The chemisorption of the reactants, intermediates, and products on the catalyst surface have been studied with INDO as well. These results may help guide the design of an improved catalyst for this important reaction.

- 287. The Molecular Precursor Strategy for the Production of Superconducting Oxides**
K.C. Caulton **\$159,000**
Department of Chemistry **(14 mo.)**

The project objective is to use the general principles of molecular metal alkoxide chemistry to synthesize mixed-metal (ternary) alkoxides $\text{M}_a\text{M}'_b\text{M}''_c(\text{OR})_n$ and to convert these at low temperatures to ternary metal oxides of the general type shown to be high-temperature superconductors. The method is generalized to the synthesis of heterometallic oxo/alkoxides, the oxo group in the molecular preceramic being incorporated via a variety of modern synthetic reagents: ${}^1\text{BuO}_2{}^1\text{Bu}$, ${}^1\text{BuO}_2\text{H}$, or $({}^1\text{BuO}_2)_2\text{CO}$. The methodology is considerably more general than simply a new route to $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, and it is therefore proposed to produce heterometallic oxides from soluble molecular precursors containing mixed oxidation states of manganese, chromium, or vanadium. Conversion of the molecular preceramic to a mixed-metal oxide will employ not only conventional sol/gel/calcining methodology, but also nontraditional energy sources such as photolysis and ultrasonication. In this fashion, conversion to not only bulk solid, but also direct formation of thin superconducting oxide layers is enabled, the latter from dip-coated substrates.

- 288. Metal Alkoxides: Models for Metal Oxides**
M.H. Chisholm **\$95,000**
Department of Chemistry

Structural analogies between polynuclear metal alkoxides and metal oxides have been noted, with the former providing models for subunits within the extended networks of the latter. An

extensive organometallic chemistry supported by alkoxy ligands is emerging. Their facile interconversion between terminal and bridging positions and between σ^2 and $(\sigma^2 + \pi^2)$ donors allows for easy uptake and release of substrate molecules. Key observations during the 1985 to 1988 period are: (1) the cleavage of $\text{C}\equiv\text{O}$ to carbido- and oxo-tungsten alkoxide clusters; (2) the coupling, co-coupling, and sometimes metathesis-like reactions ($\text{M} = \text{W}$) between $\text{C}\equiv\text{C}$, $\text{C}\equiv\text{N}$, and $\text{M}\equiv\text{M}$ bonds in $\text{M}_2(\text{OR})_6$ compounds; (3) unusual α - and β -hydrogen effects in dinuclear alkyl-alkoxides of molybdenum tungsten; (4) the isolation of Mo-Mo quadruply bonded compounds supported by alkoxide ligands; (5) syntheses of hydridoditungsten alkoxide anions $\text{W}_2(\mu\text{-H})(\text{OR})_8^-$ (which have been isolated as sodium salts), new nitrido and amido clusters $\text{Mo}_4(\mu_3\text{-N})_2(\text{OPr}^i)_{12}$ and $\text{W}_3(\mu_3\text{-NH})(\text{OPr}^i)_{10}$ (which may provide models for the Haber synthesis of NH_3 from N_2 and H_2), and alkyl/aryl-containing tri- and tetranuclear alkoxide clusters; and (6) the activation of ethylene to form a novel dimetallacycle involving both a μ -alkylidyne functionality and a terminal alkyl ligand. The latter reaction proceeds according to the stoichiometry of the equation: $\text{W}_2(\text{OR})_6 + 3\text{C}_2\text{H}_4 \rightarrow \text{W}_2(\text{OR})_6(\mu\text{-CCH}_2\text{CH}_2\text{CH}_2) + \text{C}_2\text{H}_6$. In the presence of H_2 the system becomes catalytic in the formation of ethane via a $\text{W}_2(\mu\text{-CMe})$ alkoxide containing species.

- 289. A Model Approach to Vanadium in Crude Oils and Refining**
G. Christou **\$171,700**
Department of Chemistry **(18 mo.)**

The vanadium impurities of crude oils consist of vanadyl (VO^{2+}) units bound to porphyrin and nonporphyrin organic groups. During HDS processes, these are converted to insoluble vanadium sulfides which contribute to poisoning of the Mo/Co catalyst. The project objective is the synthesis and study of discrete V/S aggregates of various nuclearity, to model intermediate stages of vanadium sulfide formation and to provide mechanistic insight into the polymerization process. An extensive chemistry of vanadium bound to sulfide and/or thiolate groups has now been established. Recent focus has been on the preparation of species containing the $\text{V}_3(\mu_3\text{-S}^{2-})$ moiety already identified in $[\text{V}_4\text{S}_2(\text{SCH}_2\text{CH}_2\text{S})_6]^{2-}$. These complexes and other species can be employed to propose various means by which the mononuclear VO^{2+} impurities may be sequentially de-ligated and aggregated by S^{2-} incorporation to yield higher nuclearity V/S species intermediate to vanadium sulfide formation. Also recently isolated is the mononuclear V^{IV} species $\text{V}(\text{SBU}^i)_4$. This product supports the suggested initial conversion of VOL_4 impurities to VL_4 by oxide abstraction by the H_2 atmosphere during HDS. This increases the number of established potential transformations of VOL_4 units from previous synthetic work. The $\text{V}(\text{SBU}^i)_4$ complex (and others) are also being reacted with Mo/S sources seeking previously unknown mixed-metal V/Mo/S species. These are meant to explore the possibility that initial interactions of V/S products with the molybdenum catalyst may be yielding a mixed-metal sulfide phase on the catalyst surface, which may still be active prior to deactivation by excessive metal loading.

290. Free-Radical and Concerted Reactions in Coal Liquefaction
J.J. Gajewski, K.E. Gilbert **\$83,000**
Department of Chemistry

Previous work has focused on the high-temperature behavior of coal liquefaction model compounds like diaryl hydrocarbons and ethers as well as tetralins. The chemistry has been demonstrated to be that of long chain radical reactions, but the rearrangement of the mono- and di-phenyltetralins to indanes defies simple description. The chains appear short, but the kinetics have yet to be interpreted reasonably. Recent efforts have begun to focus on the gas phase reactions of tetralin itself in an effort to quantify the efficiencies of processes described by Trahanovsky and Bergman. The molecular mechanics program used to calculate heats of formation of conjugated pi systems has evolved through incorporation of an open shell pi scf subroutine in order to handle radical systems. A further evolution is the use of charge-charge interactions instead of bond dipole interactions; this allows pi stacking interactions in donor acceptor complexes to be examined. An evaluation of the current parameterization of metal ligand bonds is in progress by systematic examination of the Cambridge data base.

Indiana University-Purdue University
Indianapolis, Indiana 46223

291. Studies of Metal-Ammonia Interactions with Aromatic Substrates
P.W. Rabideau **\$82,000**
Department of Chemistry

There is a considerable amount of interest in dissolving metal reduction and reductive alkylation since these processes promote the solubilization of coal and related fossil fuels. Research is directed toward a better understanding of these reduction pathways. Polynuclear aromatic hydrocarbons (PAs) are used as substrates since these compounds serve as model compounds for coal because of their presence in the coal structure (albeit not in monomeric form). Attention is also directed toward the structure and reactivity of hydroaromatics, and these latter compounds are quite important because of their role as hydrogen donors in coal liquefaction. The intermediates in these reactions are monoanions and dianions, and their structure has been studied by both theoretical methods (semiempirical molecular orbital calculation) and spectroscopic techniques (nuclear magnetic resonance, NMR). This has revealed some interesting results with respect to the position of the alkali metal counterions. Calculations do not predict a symmetrical over and under placement of the metal ions as has previously been believed solely on the basis of electrostatics. Studies are also continuing concerning the conformational analysis of partially unsaturated six-membered rings (i.e., hydroaromatics) by carbon and proton NMR.

University of Iowa
Iowa City, Iowa 52242

292. Synthesis and Chemistry of Cationic d⁰ Metal Alkyl Complexes
R.J. Jordan **\$160,000**
Department of Chemistry **(18 mo.)**

The objective of this research is to understand the chemistry of new types of cationic, d⁰ organometallic complexes of Group IV-VI metals that incorporate important features of heterogeneous catalysts, such as high steric and electronic unsaturation, terminal and bridging oxo ligands, and alkoxide groups. The scope and mechanisms of the olefin insertion and oxidation reactions, and H₂ and C-H bond activation of highly electrophilic metal centers will be studied, to increase understanding of (1) the generation, structures, and reactivity of olefin polymerization and oxidation catalysts and (2) the development of new catalysts and synthetic reagents of importance to efficient hydrocarbon utilization.

University of Kentucky
Lexington, Kentucky 40506-0055

293. Metallacumulenes and Carbide Complexes
J.P. Selegue **\$113,023**
Department of Chemistry

The synthesis, structure, and reactivity of metallacumulenes and carbide complexes, molecules containing cumulated chains of carbon atoms terminating at transition metal atoms at one or both ends, are under investigation. These compounds are models for carbides and derived fragments that are formed on catalyst surfaces during carbon monoxide and acetylene conversion reactions. It is believed that the tautomerization of side-bonded alkyne complexes, M(HC≡CR), into end-bonded vinylidene complexes, M=C=CHR, plays a role in transition-metal-mediated reactions of alkynes, and this tautomerization and its reverse on molybdenum and tungsten centers are being studied. For example, treatment of [Mo(HC≡CMe₃)(PMe₂Ph)₂(Cp)]⁺ with carbon monoxide converts it into the vinylidene complex [Mo(C=CHCMe₃)(CO)(PMe₂Ph)₂(Cp)]⁺ whereas the reverse reaction occurs when [Mo(C=CHCMe₃)(CO)P(OMe)₃(Cp)]⁺ is warmed above 0°C. Recently, complexes with both alkyne and vinylidene ligands have been examined. Also being studied are reactions of cumulated alkylidene ligands. Oxidation of the vinylidene complex [Fe(C=CHMe)(dppe)(Cp)]⁺ (dppe = Ph₂PCH₂CH₂PPh₂) with PhIO or Cu(II) produces [Fe₂(μ-C₄Me₂)(dppe)₂(Cp)₂]²⁺, in which a bond is regioselectively formed between the β-carbon atoms of the two vinylidene ligands. Since the vinylidene ligands are produced by tautomerizing propyne on iron, this reaction demonstrates a complete reversal of selectivity induced by coordination to iron. Metal carbide complexes are closely related to metallacumulenes. The first heteronuclear μ₂-carbide complex was prepared by reacting [W(≡CEt)(OCMe₃)₃] with [Ru(C≡CMe)(CO)₂(Cp)] to give [(Cp)(CO)₂Ru-C≡W(OCMe₃)₃] and 2-pentyne.

Lehigh University
Bethlehem, Pennsylvania 18015

294. Infrared Study of Carbon Deposits on Bimetallic Catalysts

R.P. Eischens **\$83,949**
Department of Chemistry

The project objectives are (1) to determine the nature of carbon deposits on alumina-supported bimetallic catalysts and (2) to determine whether the species that produce infrared bands at 1,585 and 1,460 cm^{-1} are caused by carbon-oxygen vibrations similar to the asymmetric and symmetric vibrations of carboxylate ions. The objective of relating the bands to catalyst performance requires special apparatus in which a dedicated infrared spectrometer is equipped with a microbalance so that the weight of carbon deposits can be monitored simultaneously with observation of the infrared spectra. This apparatus is now being constructed.

295. Mechanisms and Controlling Characteristics of the Catalytic Oxidation of Methane

K. Klier, G.W. Simmons, **\$116,318**
R.G. Herman
Department of Chemistry

The activation of methane (CH_4) and dichloromethane (CH_2Cl_2) on Pd/Cl/O overlayers was studied by LEED-Augger-TPD and HREELS. Dichloromethane, which is a compound used to control oxidation of methane to formaldehyde over real palladium catalysts, was found by HREELS to completely dissociate on Pd(100) with the formation of Pd-C, Pd-H, and Pd-Cl vibrational modes and no C-Cl or C-H modes. The hydrogen and surface carbon can be selectively oxidized, leaving a partially immobile chlorine overlayer that determines the sizes of palladium metal atom ensembles that are available for further chemisorption. The chlorine overlayer controls the selectivity of oxidation of surface carbon to CO or CO_2 . At Cl/Pd(100) surface coverage $\theta_{\text{Cl}} = 0.20$ to 0.22, the oxidation goes almost exclusively to CO; at $\theta_{\text{Cl}} < 0.05$ the oxidation product is CO_2 . A surface phase diagram of O/Pd(100) has been constructed for a temperature range 293 to 800 K, and all structures characterized by LEED, HREELS, and TPD. The previously observed $R\sqrt{5} \times \sqrt{5}$, $\theta_o = 0.8$, structure displays low (350 cm^{-1}) and high (430 cm^{-1}) frequency vibrational transitions, which correspond to modes associated with off-center oxygen in four-fold holes in the Pd(100) surface. Semi-empirical Wilson F-G method accounts for the frequencies and intensities of these two modes.

Louisiana State University
Baton Rouge, Louisiana 70803-7303

296. Direct Alcohol Synthesis Using Modified Cobalt Catalysts

G.L. Griffin **\$105,000**
Department of Chemical Engineering

The preparation, characterization, and kinetic activity measurements of a sequence of Cu : ZnO and Cu : Co : ZnO : Al_2O_3 catalysts for alcohol synthesis via CO hydrogenation are described. For binary Cu : ZnO catalysts prepared by various precipitation methods, methanol is the only reaction product, and its rate of formation is proportional to the metallic copper surface area of the catalysts. For a Cu : Co : ZnO : Al_2O_3 : K

catalyst, a Schulz-Flory-Anderson distribution of higher alcohols forms the major product group, with smaller amounts of hydrocarbons and methanol being formed in parallel. The overall yield of higher alcohols increases linearly with CO conversion, while the selectivity for hydrocarbon products increases slightly with conversion. The product alcohols do not undergo a significant degree of secondary reaction at the concentrations formed under these conditions. Temperature programmed desorption experiments using both H_2 and CO reveal the presence of distinguishable copper and cobalt adsorption sites, with some limited evidence for interaction between sites. The overall results are consistent with a mechanism for higher alcohol synthesis that involves chain growth of a common surface alkyl intermediate at a surface-modified cobalt site, followed by a chain termination step which determines whether the final product desorbs as an alcohol or hydrocarbon.

University of Louisville Research Foundation
Louisville, Kentucky 40292

297. Synthesis and Properties of Metallo-carboxylic Acids

D.H. Gibson **\$61,056**
Department of Chemistry

The goals of this research are (1) to establish general synthetic routes to metallo-carboxylic acids and some of their derivatives and (2) to establish the reactions that are characteristic of metallo-carboxylates. Recent efforts have focused on the syntheses of metallo-carboxylate anions, $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COOM}$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$ and $1/2\text{Ca}$). All of these transfer oxide efficiently to trityl cation and to metal carbonyl cations such as $\text{Mn}(\text{CO})_5(\text{PPh}_3)^+$, whereas the course of reactions with organic alkylating agents (such as methyl iodide or methyl triflate) is determined by the counterion M. When $\text{M} = \text{Li}$ or $1/2\text{Ca}$, oxide transfer is predominant, whereas with the potassium salt, alkylation is the predominant reaction; the sodium salt is intermediate between these two extremes. Loss of CO_2 does not occur with these metallo-carboxylate anions. Reaction of the potassium salt with triphenyltin chloride gives the CO_2 -bridged bimetallic compound in high yield; the x-ray crystal structure of this product shows bonding of the tin atom to both oxygens, but one is more strongly bonded than the other. Studies of the reactions of the metallo-carboxylates with other electrophiles are in progress.

University of Massachusetts
Amherst, Massachusetts 01003

298. Surface Analyses and Modeling of Rate Multiplicity and Instabilities in Catalytic Reactions

M.P. Harold **\$95,825**
Department of Chemical Engineering **(16 mo.)**

A large class of catalytic reactions exhibits rate multiplicity and oscillatory behavior. This study addresses whether such phenomena have an intrinsic kinetic origin. The first phase of the project couples nonlinear mathematical tools with kinetics experiments of the oxidations of carbon monoxide and formaldehyde on a single platinum wire. Operating regimes in which rate multiplicity exists are determined by locating the bifurcation (ignition and extinction) points. At atmospheric pressure,

CO oxidation has a cusp-shaped bifurcation map (multiplicity region). Wire temperature nonuniformities transform the map into one characteristic of the pitchfork singularity. Infrared photography is used to measure the wire temperature during the spatially nonuniform states. A wide range of total pressures (to 0.01 torr) is spanned to assess the impact of transport limitations. Singularity theory techniques are used to analyze intrinsic rate multiplicity data for kinetic model discrimination. The second phase involves the development of a scanning Fourier transform infrared emission technique to measure the temporal and spatial dependence of the sorbed species for CO oxidation and CO reduction by NO on a platinum foil. *In situ* measurement of the sorbed species will provide pertinent data for the kinetic modeling, and help to determine the mechanisms responsible for the instabilities.

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

**299. Chemistry of Bimetallic Cyclopentadienyl
Complexes**

R.R. Schrock **\$122,400**
Department of Chemistry

This work continues to explore the chemistry of homo- and heterobimetallic complexes containing peralkylated cyclopentadienyl rings linked via a relatively flexible CH₂CH₂ bridge, with the expectation that two linked metals can behave cooperatively in catalytic reactions in ways that cannot be duplicated in systems containing monometallic catalysts. Recent examples of potentially interesting complexes in this class are [WO₂Cl][η⁵-C₅Et₄CH₂CH₂-η⁵-C₅Me₄][Co(CO)₂] and [WMe₄][η⁵-C₅Et₄CH₂CH₂-η⁵-C₅Me₄][RhMe₂(PMe₃)]. Routes to the permethyl analogs and related species have been developed. Of special interest are complexes that contain all the elements necessary for the bimolecular heterometallic activation of CO, e.g., [WH₃(triflate)₂(PMe₃)][η⁵-C₅Me₄CH₂CH₂-η⁵-C₅Me₄][RhMe(CO)(PMe₃)] or [WH³(triflate)₂(PMe₃)][η⁵-C₅Me₄CH₂CH₂-η⁵-C₅Me₄][Rh(MeCO)(I)(PMe₃)]. A significant number of ditungsten complexes have been prepared in the expectation that binding of dinitrogen between two metals in the "linked" system would be more favorable. So far, however, a molecule such as [WMe₃]₂(η⁵-C₅Me₄CH₂CH₂-η⁵-C₅Me₄)(μ-N₂), an analog of the known dinitrogen complex, [WCp^{*}Me₃]₂(μ-N₂), has not been prepared.

**University of Minnesota
Minneapolis, Minnesota 55455**

**300. Homogeneous-Heterogeneous Combustion:
Chemical and Thermal Coupling**

L.D. Schmidt **\$76,300**
Department of Chemical Engineering and Materials Science

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 NH₃ + O₂ → NO,

CH₄ + O₂ → CO, and CH₄ + NH₃ + O₂ → 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 will also be used to simulate behavior observed experimentally. 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.

**University of Missouri
Columbia, Missouri 65211**

**301. Late Transition Metal μ-Oxo and μ-Imido
Complexes**

P.R. Sharp **\$107,872**
Department of Chemistry

Late transition metal oxo and imido complexes may be considered as models for oxygen adatom and nitrenes on late transition metal surfaces. Such species are readily formed on the surface of late transition metals and are believed to be important in many reactions catalyzed by late transition metals. This project is directed at (1) the development of synthetic strategies for oxo and imido complexes of late transition metals and (2) an exploration of their reactivity. Synthetic approaches will include deprotonation of hydroxo and amido complexes, oxygen atom and nitrene insertion into metal-metal bonds, and reduction of dimeric dioxygen, azo, and nitroso complexes. Reaction studies will examine the oxygen atom and nitrene transfer capabilities of the oxo and imido complexes.

**National Bureau of Standards
Gaithersburg, Maryland 20899**

**302. Structure and Reactivity of Chemisorbed Species
and Reaction Intermediates**

T.E. Madey **\$140,000**
Surface Science Division

This project concerns the structure and reactivity of adsorbed molecules on single-crystal metal and semiconductor surfaces and on high area catalysts, using a variety of methods. Recent activities include a broad program to study the surface chemistry and physics of monolayer thin films of platinum on tungsten. This involves the structure of the films, the electronic properties (using synchrotron radiation), the chemisorption behavior, and catalytic reactivity. Results clearly show that a single platinum monolayer has surface chemical and electronic properties that are vastly different from either platinum or tungsten alone. Neutron inelastic scattering is used to study adsorption on Raney nickel made from isotopically pure nickel-60. Because this material has a very low neutron scattering cross section, we will enhance surface sensitivity for adsorbed molecules by making the bulk transparent. The electron stimulated desorp-

tion ion angular distribution (ESDIAD) method is being used to study the surface chemistry of metals and semiconductors. Interesting structures are found for the dissociation products of HF and H₂O on planar and stepped Si surfaces. The first measurements of negative-ion ESDIAD (negative F ions from adsorbed PF₃ and hexafluoracetone) are providing new insights into the structures of fluorine-containing molecules on metal surfaces.

University of Nevada
Reno, Nevada 89557

- 303. High-Temperature Chemistry of Aromatic Hydrocarbons**
L.T. Scott **\$150,000**
Department of Chemistry **(18 mo.)**

This work focuses on some elementary chemical processes that concern the uncatalyzed conversions of coal, particularly its gasification and liquefaction. The molecular reaction chemistry occurring during the heating of coals to high temperatures will be studied, as it pertains to the thermal transformations of primary subunits in coal, comprised of benzenoid rings and related aromatic structures (all prominent in the molecular architecture of coal). The work aims to uncover the principal reaction channels available to polycyclic aromatic hydrocarbons, and to understand the rearrangements and interconversions that occur in thermal activation.

State University of New York/Buffalo
Buffalo, New York 14260

- 304. Mechanistic Examination of Organometallic Electron-Transfer Reactions**
J.D. Atwood **\$150,000**
Department of Chemistry **(16 mo.)**

This research involves a mechanistic examination of organometallic reactions that occur through electron transfer. It is centered on reactions of metal carbonyl anions with metal carbonyl cations and with metal dimers. The reactivity of the metal carbonyl anion is strongly related to the counter cation used. The reaction of anions with cations appears (in some cases) to involve nucleophilic attack of the metal carbonyl anion on a carbon of the cationic carbonyl before electron transfer. An especially interesting example is the very rapid reaction of Mn(CO)₆⁺ with Re(CO)₅⁻ that initially appears to give Mn(CO)₅⁻ and Re(CO)₆⁺. An infrared stopped-flow spectrophotometer is under construction to further examine this reaction. Reactions of metal carbonyl anions with metal carbonyl dimers result in electron transfer that may be accompanied by ligand redistribution reactions. The nature of the ligand is crucial in whether or not ligand redistribution reactions occur. Isotopic labeling and infrared stopped-flow techniques are being used to define the mechanism of this reaction.

University of North Carolina
Chapel Hill, North Carolina 27514

- 305. Reductive Coupling of Carbon Monoxide to C₂ Products**
J.L. Templeton **\$94,965**
Department of Chemistry

The theoretical and experimental aspects of carbyne-carbonyl coupling reactions are being studied. Progress has been made in understanding details of coupling reactions involving metal-carbon multiple bonds. Stepwise conversion of a vinylidene ligand to a carbyne by electrophilic addition at C_β, followed by coupling with carbon monoxide and then electrophilic addition to the ketenyl oxygen, yields a C₂ alkyne product. Attempts are being made for coupling along a parallel path by conversion of a terminal carbonyl ligand to an alkoxy-carbyne adjacent to a second carbonyl ligand. Protonation of an anionic carbonyl complex to form a hydroxycarbyne is central to this scheme, but initial efforts are directed toward preparation of a covalent O-X link from a terminal carbonyl to larger Group IV reagents. Both electronic and steric factors will be controlled to foster electrophilic attack at oxygen. A rare terminal carbyne carbonyl derivative of tungsten was synthesized, and studies of nucleophilic and electrophilic reactions of the W≡CH unit are planned.

Northwestern University
Evanston, Illinois 60201

- 306. Solid-State, Surface, and Catalytic Studies of Oxides**
H.H. Kung **\$109,440**
Department of Chemical Engineering

The selective conversion of low-priced saturated hydrocarbons to unsaturated hydrocarbons, aromatics, alcohols, aldehydes, or acids that are of much higher value 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 reactions. 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. Single crystal ZnO surfaces are used to study methanol decomposition under near-atmospheric pressure. It is found that the zinc-polar surface is much more active than the oxygen-polar surface. The latter is essentially inactive. Thus the ability for the metal cations in the surface to interact with the methanol molecule is a necessary condition for catalytic activity. The oxidative dehydrogenation of butane and propane over magnesium vanadates has also been studied. It is found that magnesium orthovanadate is the selective catalyst. Magnesium metavanadate and pyrovanadate are nonselective. By studying other vanadates in which magnesium is substituted by lanthanum, it is concluded that the orthovanadate structure in which oxygen ions are present in the (VO₄) units is an important factor. In addition, under appropriate conditions, the catalyst also serves as a source of reactive intermediates for the gas phase reaction.

**307. Supported f-Element Organometallic Complexes:
Surface Chemistry and Catalysis**
T.J. Marks, R.L. Burwell, Jr. **\$91,000**
Department of Chemistry

The project objective is to understand the dramatic changes in catalytic activity that occur when actinide or early transition metal organometallic molecules are adsorbed on Lewis acid metal oxide and metal halide surfaces. The approach involves integrated surface chemical (product analysis, isotopic labeling), catalytic (chemoselectivity, kinetics), and spectroscopic (CPMAS NMR, FT-IR) studies of selected actinide and group 4 organometallic molecules adsorbed on high surface area Al_2O_3 , SiO_2 , MgCl_2 , and other supports. A parallel solution chemistry effort focuses on the synthesis of new complexes that model the surface environment and test ideas about the chemistry. A detailed kinetic study has now been completed on olefin hydrogenation by $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{dehydroxylated Al}_2\text{O}_3$ ($\text{Cp}' = (\text{CH}_3)_5\text{C}_5$). There are many mechanistic similarities to Th-C hydrogenolysis patterns in solution. Furthermore, CPMAS studies reveal that unsaturated cationic complexes of the type $\text{Cp}'_2\text{ThCH}_3^+$ are formed in large quantities on Al_2O_3 surfaces. Rational synthetic routes to previously unknown f-element cations have now been developed in solution. Cationic organothorium species have also been identified for $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{MgCl}_2$, and dosing with ethylene reveals that olefin polymerization occurs exclusively at the Th-C bond.

**308. Chemical Interactions in Multimetal-Zeolite
Catalysts**
W.M.H. Sachtler **\$88,500**
Department of Chemistry

The chemistry and physics controlling the formation of metal particles in faujasite-type zeolites are studied and the results exploited for the preparation of catalysts with predetermined properties. Transition metals (TMs) are introduced into the zeolite either by ion exchange, followed by calcination and reduction, or by decomposition of metal carbonyls. After losing their ligands, TM ions tend to migrate to smaller cages. Reduction then requires high temperature and is reversible: at high T and low $p(\text{H}_2)$ the metal atoms are re-oxidized by protons and H_2 is released, which is identified by a characteristic TPD peak. Cation migration to small cages can be suppressed and their reducibility dramatically increased by first occupying these cages with cations of a second, nonreducible TM. This auxiliary element can also serve as chemical anchor and catalyst promoter. Bimetallic catalysts are prepared by controlled ion exchange/calcination aimed at locating platinum, ions in supercages, or nickel or copper ions in sodalite cages. TPR shows a profound effect of platinum on the reducibility of nickel or copper. Bimetallic particles are formed in supercages; their catalytic properties confirm predictions. Decomposing rhenium carbonyl on Pt/NaY results in PtRe particles, identified as selective catalysts for C-C fission.

**309. Structure and Chemistry of the Interaction of
Organometallics with Surfaces**
D.F. Shriver **\$102,000**
Department of Chemistry

The overall objective is to develop greater understanding of the surface organometallic chemistry of carbon monoxide, with emphasis on reactions that activate CO toward the formation of oxyanions. Focus is on processes that lead to CO cleavage

versus those that lead to CO migratory insertion, and on the nature of catalytically important ligands, C, O, and CO. Investigations into the role of electropositive promoters on CO hydroformylation by Rh/SiO_2 are under way. Current research involves a study of the nature of the interaction of ZnO_x with the rhodium catalyst and correlation of this interaction with selectivity for hydroformylation. In a separate study of cluster models for surface species, oxo-containing low-oxidation state clusters are being studied. The mode of bonding of the oxygen atom to low-oxidation state molecular clusters has many analogies to metal surfaces, and both of these systems contrast with simple metal oxides.

**University of Pennsylvania
Philadelphia, Pennsylvania 19104**

**310. Support Effects Studied on Model Supported
Catalysts**
R.J. Gorte **\$84,000**
Department of Chemical Engineering

Model catalysts consisting of thin films of Group VIII metals deposited on alumina, silica, zirconia, and magnesia 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 butane hydrogenolysis 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.

**311. Synthesis and Properties of New Preceramic
Materials**
L.G. Sneddon **\$150,000**
Department of Chemistry **(18 mo.)**

The development of new methods for the production of complex materials is one of the most important problems in modern solid-state chemistry and materials science. This project is attempting to apply the synthetic principles that have evolved in inorganic and organometallic chemistry to the production of important nonoxide ceramics, such as boron nitride, boron carbide, and metal borides. The synthetic approach is focusing on the use of transition metal catalysts to induce transformation in molecular boron-hydrogen compounds, leading to the formation of useful preceramic materials. Recent work has resulted in the production of several new polymer systems, including poly(vinylborazine) and poly(vinylpentaborane), which have proven to be high-yield precursors to boron nitride and/or boron carbide. Current work is directed toward the synthesis of new types of molecular and polymeric boron-containing species and an exploration of the solid-state properties of the ceramics which have been produced in these studies.

312. Catalytic Hydrogenation of Carbon Monoxide
B.B. Wayland **\$107,500**
Department of Chemistry

This project is focused on developing strategies to accomplish the hydrogenation of carbon monoxide to produce organic oxygenates at mild conditions. Approaches to this issue are based upon the recognition that rhodium macrocycles have unusually favorable thermodynamic values for producing a series of metallo intermediates implicated in the catalytic hydrogenation of CO. Thermodynamic and kinetic-mechanistic studies are used in constructing energy profiles for metal-promoted conversion of H₂ and CO to oxygenates, and these schemes are used in guiding the design of new metallospecies that could improve the thermodynamic and kinetic factors for individual steps in the overall process. Variation of the electronic and steric effects associated with the ligand arrays along with the influences of the reaction medium provide the chemical tools for tuning these factors. This general approach was successfully used to establish thermodynamic criteria for metal-promoted reductive coupling of carbon monoxide, which resulted in the recent observation that rhodium porphyrins can accomplish this important reaction. Current studies are directed toward the use of nonmacrocylic ligand complexes that emulate the favorable thermodynamic features associated with rhodium macrocycles, but that also manifest improved reaction kinetics.

Pennsylvania State University
University Park, Pennsylvania 16802

313. Mechanistic Studies of Carbon Monoxide Insertion into Metal-Nitrene and Metal-Carbene Bonds
G.L. Geoffroy **\$125,000**
Department of Chemistry

The reactivity of nitrene, ketene, and ketylenyl ligands on metal clusters and the cycloaddition reactions of metal carbyne complexes are being studied. The overall goal of the nitrene research is to understand the mechanism by which complexes such as Ru₃(CO)₁₂ catalyze the carbonylation of nitroaromatics to form isocyanates, carbamates, azo, and azoxy compounds. In this work, halides have been found to dramatically accelerate the formation of nitrene ligands from nitroso reagents and their carbonylation to form isocyanates, both of which are believed to be important reaction steps in the nitroaromatic carbonylation catalytic cycle. Studies are in progress to determine the mechanisms of these reactions. The carbonylation of acyl and carbene ligands is also being explored in this research. A recent significant finding is that carbon monoxide can be induced to insert into metal-acyl bonds (a long regarded forbidden reaction) by a novel oxidation/NO addition reaction sequence. The scope of this reaction is currently under investigation along with reactivity studies of the novel α -ketoacyl complexes that are formed. We have similarly found that oxidation promotes the carbonylation of carbene ligands to form ketenes. In a third area of study, the susceptibility of metal carbyne complexes to cycloaddition reactions is being explored, and a recent finding is the formation of novel metallacycles through addition of imines to the carbyne ligands in [Cp(CO)₂M≡CTol]⁺ (M = Mn, Re) complexes.

314. Determination of the Distribution of Hydrogen in Coal by FTIR
P.C. Painter **\$94,000**
Department of Materials Science and Engineering

The project objective is to characterize coal structure through the measurement of the distribution of hydrogen containing functional groups in coal. Work has broadened to include the effect of hydrogen bonding interactions on the thermodynamics of coal solutions and hence structural parameters determined by swelling and molecular weight measurements. More than 30 soluble coal extracts have now been obtained and characterized by Fourier transform infrared spectroscopy and proton nmr. Structural parameters are now being calculated. In addition, a theoretical model that accounts for the effect of hydrogen bonding on the solution thermodynamics of coal molecules has been developed and will be used to reassess the interpretation of dissolution, swelling, and molecular weight measurements.

315. Transition Metal Mediated Transformations of Unsaturated Molecules
A. Sen **\$117,000**
Department of Chemistry **(16 mo.)**

Transition metal mediated transformation of organic molecules in homogeneous solutions is of considerable scientific and practical importance because of the high efficiency, high specificity, and low energy demands often associated with such systems. The project objectives are: (1) to achieve a fundamental mechanistic understanding of a number of important systems of this type and (2) to use this knowledge to develop new and useful transition metal mediated organic transformations. The following systems are currently under study: (1) a novel palladium (II) mediated procedure for the selective functionalization of alkanes and arenes; (2) a palladium (II) catalyzed process for the copolymerization of carbon monoxide and olefins that leads to the formation of highly functionalized polymers; and (3) a procedure for the synthesis of complex organic molecules that involves the use of novel transition metal enolate complexes. These studies are expected to lead to the development of new, selective, and energy-efficient methods for the conversion of inexpensive feedstocks to useful organic and polymeric substances.

316. Characterization of Catalysts with Metal-Support Effects and of the Species Adsorbed on Their Surfaces
M.A. Vannice **\$311,000**
Department of Chemical Engineering **(18 mo.)**

The project objectives are to elucidate the chemistry involved in the creation of metal-support interactions that have a pronounced influence on adsorption and catalytic behavior and 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. The project has involved a study of heats of adsorption (Q_{ad}) of H₂, CO, and O₂ on Pt and Pd using a modified differential scanning calorimeter combined with a thermal gravimetric analysis unit. The Q_{ad} values for these three gases on Pd exhibited a similar pattern: each increased significantly as the Pd crystallite size decreased below 3 nm, and the support had little effect. A similar dependence on crystallite size does not occur for these gases on Pt, but

certain supports such as TiO_2 can decrease the CO heat of adsorption. Kinetic studies have been made on hydrogenation reactions involving aromatic hydrocarbons and the C-O bond in carbon monoxide, acetone, and crotonaldehyde. A greater than 100-fold enhancement was found for acetone hydrogenation over TiO_2 -supported Pt, similar to that for CO hydrogenation. These catalysts preferentially activated the CO bond in crotonaldehyde to give selectivities of over 35% crotyl alcohol whereas typical Pt/SiO_2 and $\text{Pt/Al}_2\text{O}_3$ catalysts produced 100% butyraldehyde. A model invoking special metal-support interface sites has been proposed to explain this selective activation of carbonyl bonds. Emphasis is now on the characterization of these adsorbed molecules using infrared spectroscopy and solid-state MAS-NMR. The latter technique will also be used to conduct Knight shift experiments on the metal (^{195}Pt) itself to determine the influence of both crystallite size and the support on conduction electrons. This approach may provide insight into the chemistry responsible for changes in catalytic activity and selectivity.

University of Pittsburgh Pittsburgh, Pennsylvania 15260

317. Studies of the Fundamental Nature of Catalytic Acidity, Sites, and Intermediates
W.K. Hall **\$105,000**
Department of Chemistry

The acidity of various solid acids (particularly H-zeolites) is being investigated using two approaches: physical measurements and catalytic reactions. Evidence of superacidity is being sought. Neopentane, because of its unique structural features, was found to be the most useful probe for the qualitative assay of the intensive factor of the acidity (i.e., the strength of the individual active Bronsted sites). The data conformed to a primary reaction step in which one CH_4 molecule was released for every neopentane decomposed. Presumably this occurred, as in liquid superacids, via a pentacoordinated carbonium ion (protonated σ -bond). A variety of solid acids are under investigation. The extensive factor of the acidity is the number of Bronsted sites per unit volume, while the intensive factor may be defined by K , the equilibrium constant, from $(\text{CH}_3)_3\text{C}^+ + \text{B}^- = \text{HB} + (\text{CH}_3)_2\text{C}=\text{CH}_2$. Qualitatively, when K is large, isobutene will be released with minimal side reactions; when it is very small the carbenium ions will be stabilized as in strong superacids. But when $.01 < K < 100$ exists, major secondary reactions (oligomerization, conjunct polymerization, and especially hydrogen transfer) will occur. Two of these conditions have been observed (the first and last), but not the stabilization of the *t*-butyl ion. Consistent results have been obtained from ^{13}C -MASNMR measurements of adsorbed 2-propanol- 2^{13}C . Evidence of surface oligomerization was obtained, but no stable monomeric carbenium ions were observed. With triphenylmethanol- ^{13}COH , the stable triphenylcarbenium ion was characterized.

318. Studies of Supported Metal Catalysts
D.M. Hercules **\$125,333**
Department of Chemistry **(16 mo.)**

The mechanism of adsorption of anions of catalytically important species on alumina surfaces has been investigated. The methodology adopted for the study was to examine the influence of the nature of the anion (MoO_4^{2-} , WO_4^{2-} , ReO_4^- , MnO_4^-) and

its degree of polymerization (e.g., MoO_4^{2-} vs. $\text{Mo}_7\text{O}_{24}^{6-}$) and the effects of buffering and competitive adsorption. The role of the isoelectric point (IEP) of the alumina in determining the adsorption mode of anions from solution has also been investigated. This has been achieved by examining the effect of additives (fluorine, magnesium) and the IEP of the alumina support and the ensuing impact on the adsorption of the metal complexes from solution. The effects of additives known to promote the hydrodesulfurization (HDS) reaction (titanium, boron) on the surface structure and reactivity of $\text{Mo/Al}_2\text{O}_3$ catalysts have been examined. The distribution of molybdenum species on the catalyst surface has been determined and the results correlated with HDS activity. The use of laser Raman spectroscopy (LRS) as a quantitative analytical tool was illustrated in the case of Mo/TiO_2 catalysts. The distribution of supported molybdenum species determined from LRS was consistent with that inferred from x-ray diffraction technique and ESCA. Results were correlated with the catalyst HDS activity. The methodology for quantitative analysis of catalyst species by LRS has been applied to a related HDS system (W/TiO_2).

319. Infrared Studies of Influence of Alkali Metals on C-O Bond in Chemisorbed Carbon Monoxide
J.T. Yates, Jr. **\$180,401**
Department of Chemistry

This research project employs reflection infrared (IR) spectroscopy to examine the details of the interaction between chemisorbed species on single crystal transition metal surfaces. The effect of electronegative poisons and electropositive promoters on the vibrational behavior of chemisorbed CO has been carefully probed, and both long-range and short-range interactions are observed. The coadsorption of xenon with chemisorbed CO has been shown to produce interesting shifts in the CO vibrational frequency because of several overlapping physical effects. Comparison of the IR spectra of species adsorbed on single crystals with IR spectra of the same species on supported metal catalysts is anticipated to yield a deeper spectroscopic understanding of catalytic chemistry. In addition to IR spectroscopy, this project involves XPS, LEED, TPD, and work function measurements on the chemisorbed layer.

Purdue University West Lafayette, Indiana 47907

320. Reduction of Aromatic Compounds Derived from Coal by Calcium
R.A. Benkeser **\$65,000**
Department of Chemistry

Calcium dissolved in ethylenediamine is very effective in reducing aromatic carboxylic acids to 1,4-dihydro products even in the absence of a proton donor like an alcohol. Thus, 2-methylbenzoic acid was reduced to 2-methyl-1,4-dihydrobenzoic acid in 95% yield. Attention was directed next to phenylacetic acid, 2-phenylpropanoic acid, and 2-methyl-2-phenylpropanoic acid. The objective was to ascertain what effect an additional methylene group between the aromatic ring and the carboxyl group would have on the course of ring reduction. Preliminary data indicate that the additional methylene group has a profound effect. In the reduction of phenylacetic acid, the principal product was not a dihydro compound but rather 1-cyclohexenylacetic acid. A large amount of starting material was recovered.

The results with 2-phenylpropanoic acid were similar. The principal reduction product was 2-(1-cyclohexenyl)-2-methylpropanoic acid. Again, a considerable amount of starting material was recovered. The reduction of 2-methyl-2-phenylpropanoic acid followed a different course. Very little starting material was recovered and a major product was 2-(1-cyclohexenyl)-2-methylpropanoic acid. The recovery of large amounts of starting material in the first two cases is attributed to the reactive hydrogens on the methylene group. There is evidence that these hydrogens participate in the protonation of anion intermediates. A phenyl group attached to a carbanion-like species is reluctant to take on additional electrons.

**Rensselaer Polytechnic Institute
Troy, New York 12180**

**321. Selective Transformations of Carbonyl Ligands
to Organic Molecules**
A.R. Cutler **\$110,000**
Department of Chemistry

High diastereofacialselectivity has been observed in reducing the alkoxy carbene complexes $\text{Cp}[\text{P}(\text{OR})_3](\text{CO})\text{Fe}=\text{C}(\text{OCH}_3)\text{CH}_3^+$ ($\text{R} = \text{Me}, \text{Ph}$) to $\text{Cp}[\text{P}(\text{OR})_3](\text{CO})\text{FeCH}(\text{OCH}_3)\text{CH}_3$, with $(\text{PPh}_3\text{CuH})_6$ affording $\geq 100:1$ selectivity. An x-ray structure determination of the $\text{P}(\text{OPh})_3$ -containing carbene complex indicates that a phenyl ring sterically shields one face of the carbene ligand. The $\text{Rh}(\text{I})$ -catalyzed hydrosilylation of the acetyl complexes $\text{Cp}[\text{P}(\text{OR})_3](\text{CO})\text{Fe}-\text{COCH}_3$ affords $\text{Cp}[\text{P}(\text{OR})_3](\text{CO})\text{Fe}-\text{CH}(\text{OSiHR}_2)\text{CH}_3$, also with high diastereofacialselectivity. One- and two-dimensional NMR spectral studies on the μ -vinyl $\text{Fp}-\text{CH}=\text{CH}_2(\text{Fp})^+$ have been used to probe its fluxionality. The η^5 -indenyl complex $\text{In}(\text{L})(\text{CO})\text{Ru}-\text{CH}_2\text{OCH}_3$ undergoes carbonylation under mild conditions to give $\text{In}(\text{L})(\text{CO})\text{Ru}-\text{COCH}_2\text{OCH}_3$ (the first example of carbonylating alkoxy methyl complexes cogenetic to $\text{Fp}-\text{CH}_2\text{OR}$). The reaction chemistry of the phosphide-containing acetyl complexes $\text{Cp}(\text{PPh}_2)(\text{CO})\text{Fe}-\text{COCH}_3\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) is being studied; preliminary results are consistent with both O- and P-alkylation with MeOTf and MeI , respectively, and O-metalation with Et_2AlCl , for example. The goal is to activate the acetyl ligand at the anionic metal center with the appropriate electrophile, to reduce this carbenoid center, and to subsequently carbonylate the anionic alkyl complex (e.g., $\text{Cp}(\text{PPh}_2)(\text{CO})\text{Fe}-\text{CH}(\text{OAlEt}_2)\text{CH}_3$). Synthetic and mechanistic studies on the reactions between $\text{In}(\text{CO})_2\text{Fe}\cdot\text{Li}^+$, Na^+ , and $\text{In}(\text{CO})_2\text{Fe}-\text{CH}_2\text{R}$ ($\text{R} = \text{Ph}, \text{CH}_3, \text{OMe}$) focus on the equilibrium between $\text{In}(\text{CO})_2\text{Fe}(\mu\text{-CO})(\mu\text{-C}(\text{O}^-)\text{CH}_2\text{R})$ and $\text{In}(\text{CO})\text{Fe}(\mu\text{-CO})_2\text{FeIn}(\text{COCH}_2\text{R})$.

**University of Rochester
Rochester, New York 14627**

322. Transition Metal Activation and Functionalization of Carbon-Hydrogen Bonds
W.D. Jones **\$87,400**
Department of Chemistry

The investigation of homogeneous C-H bond activation by $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)$ 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. Interestingly, the preference for $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_3)(2\text{-furyl})\text{H}$ 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. It was also found that the phosphine plays a role in the stability of the phenyl hydride complexes, with PPh_3 being the least stable and PMe_3 the most stable. The steric and electronic effect of the phosphine has been found to contribute to the stability of the complex. It was also discovered that $\text{Fe}(\text{PMe}_3)_2(\text{CNR})_3$ can catalyze the insertion of isonitrile into aromatic C-H bonds. Visible light is used to dissociate an isonitrile ligand from the complex, and low concentrations of added isonitrile are used to increase efficiency. Indoles are catalytically produced by an intramolecular insertion reaction of ortho-methylarylisonitriles using $\text{Ru}(\text{dmpe})_2\text{H}_2$ as catalyst.

**University of South Carolina
Columbia, South Carolina 29208**

323. Ligand Transformations and Catalysis by Transition Metal Cluster Compounds Containing Sulfur
R.D. Adams **\$96,603**
Department of Chemistry

This study is focused on the transformation behavior of nitrogen-containing hydrocarbon molecules at multinuclear metal sites in transition metal cluster compounds. The nature of metal-induced C-H and C-N cleavage reactions is a principal interest. A catalytic process that produces the exchange of alkyl groups between tertiary amines by carbon-nitrogen bond cleavage reactions was recently discovered. Evidence that indicates the involvement of secondary dialkylamino carbene ligands in a sulfur-containing osmium cluster has been obtained. Further mechanistic studies and efforts to produce other related catalysts are being made. These studies may lead to the discovery of catalysts that can produce the hydrodenitrogenation reaction under mild conditions.

**SRI International
Menlo Park, California 94025**

324. Interaction of Carbon and Sulfur on Metal Catalysts
J.G. McCarty **\$82,259**
Materials Research Laboratory

This project examines the effect of chemisorbed sulfur on the thermodynamics and reactivity of surface carbon for both dispersed and well-characterized metallic catalysts of commercial interest. An automated, external gas-recirculating, microreactor system designed specifically for measurement of carbon isosteres on metal catalysts has been assembled, tested, calibrated, and successfully operated. The discharge ionization detector essential to the success of the thermodynamic measurements has been calibrated for hydrogen and found to have a sensitivity of about 0.5 ppm for H_2 in a helium carrier. The gas chromatograph used in the studies of carbon and sulfur interaction on dispersed catalysts is capable of detecting levels below 1 ppm of methane, water vapor, oxygen, nitrogen, carbon monoxide, carbon dioxide, ethane, ethene, and acetylene, in

addition to hydrogen. A 2 wt% platinum catalyst with a moderate (80 m²/g) surface area alumina support has been synthesized and characterized and is under study in the new thermodynamics system. Thermally stabilized, clean fused iron catalysts and those with uniform half-monolayer coverage with chemisorbed sulfur have been prepared in a separate sulfur treatment system. These catalysts, along with a well-characterized 5 wt% nickel on a alumina catalyst which will serve as a reference catalyst for the C-S interaction system, are available for further experimentation. Measurement of carbon deposition isosteres, CO and H₂ chemisorption isosteres, and carbon hydrogasification on the clean platinum catalyst is in progress. Preliminary results show a heat of formation of about +50 kJ/mol for low carbon coverage.

Stanford University Stanford, California 94305

325. *Catalytic Steam Gasification of Carbon*
M. Boudart \$120,000
Department of Chemical Engineering (17 mo.)

Unsupported tungsten carbide powders, W₂C and WC, with up to 100 m²g⁻¹ were prepared and characterized by x-ray diffraction, chemisorption of carbon monoxide, and temperature programmed reduction in H₂/He. Posttreatment in mixtures of CH₄/H₂ indicated that the surface of fresh samples was not depleted of carbidic carbon and had very little polymeric carbon. Fresh samples of tungsten carbides catalyze the hydrogenolysis of neopentane, with a turnover frequency close to that found for supported ruthenium. After exposure of tungsten carbides to dioxygen, residual surface oxygen can be titrated by reaction with H₂ at room temperature. Surface oxygen depresses the hydrogenolysis of neopentane but triggers its isomerization to isopentane. The role of oxygen in the isomerization is explained by its spectator role as in the metathesis of alkenes. The turnover frequency for the reaction between H₂ and O₂ for WC is comparable to that for platinum whereas W₂C is an order of magnitude less active than WC.

326. *Molecular Beam Studies of the Dynamics and Kinetics of Heterogeneous Reactions on Single-Crystal Surfaces*
R.J. Madix \$136,000
Department of Chemical Engineering

By using molecular beams of alkanes, it was shown previously that C-H bonds can be activated in the collision with both Ni(100) and Ir(110) surfaces by translational energy far below the bond dissociation energy. In order to better compare the intrinsic reactivity of metals for alkane activation, the dynamics of alkane activation of Pt(111) was examined. In these studies, the translational energy dependence of both the dissociative and nondissociative sticking probabilities of ethane and methane between kinetic energies of 3.5 and 120 kJ/mol were determined. Ethane is less reactive on Pt(111) than on Ni(100). At a normal kinetic energy of 90 kJ/mol, ethane adsorbed dissociatively with an initial sticking coefficient of 0.09, compared to 0.2 on Ni(100); activation of the C-H bond occurs by direct collisional activation. Adsorption into the molecular state decreases with both incident kinetic energy and surface temperature, which is consistent with a trapping-dominated process. Scattering distributions from a Pt(111) surface at 500 K show trap-

ping at 10 kJ/mol and direct inelastic scattering above 75 kJ/mol. Methane can be dissociated observably at kinetic energies above 50 kJ/mol, and the reaction probability shows a logarithmic dependence on the kinetic energy. This dependence is similar to that observed on Ni(111) and W(110), and has been explained by quantum mechanical tunneling through the activation barrier. Adsorption into the molecular state (1) occurs with near unit efficiency at 95 K and decreases with both beam energy and surface temperature (as with methane), and (2) scales well with the normal component of the kinetic energy as expected for simple trapping theories.

Syracuse University Syracuse, New York 13244

327. *Metal-Support Interactions: The Effect of Catalyst Preparation on Catalytic Activity*
J.A. Schwarz \$81,000
Department of Chemical Engineering and Materials Science

Research efforts have been focused on the effect of catalyst preparation on catalytic activity for the Ru/Al₂O₃ system. Low weight loading catalysts derived from ruthenium nitrosyl nitrate were prepared by two methods in order to assess the impact of preparation procedures on catalyst performance. Catalysts prepared by wet impregnation have a lower temperature methane peak in TPR experiments, lower activation energies for CH₄ formation, and less residual surface carbon after steady-state kinetics compared to those prepared by incipient wetness. The most common metal salt precursor for this system is ruthenium trichloride, however residual chloride is known to block the adsorption of CO. To study the impact of chloride ions on the catalyst surface, a series of RuCl₃/Al₂O₃ catalysts were prepared by incipient wetness. The reduced catalysts were washed in a dilute ammonia solution to remove the chloride. These washed samples have lower peak temperatures for CH₄ in TPR experiments and lower activation energies compared to the unwashed catalysts. The effect of reducing agents present in the impregnating solution was examined by adding hydrazine to reduce the ruthenium metal to the 2+ oxidation state. Washing in ammonia removed all of the chloride from the low weight loading catalysts. In general, the Ru²⁺ catalysts have a higher methanation activity than their Ru³⁺ counterparts.

University of Texas Austin, Texas 78712

328. *Study of Synthesis Gas Conversion over Metal Oxides*
J.G. Ekerdt \$127,000
Department of Chemical Engineering (24 mo.)

The project objective is to develop an understanding of (1) the causes for catalytic activity and selectivity and (2) the effects of metal oxide structure and acidic and basic additives during CO hydrogenation over metal oxides. Research has focused on synthesis gas conversion over zirconium dioxide to produce branched hydrocarbons and alcohols (i.e., isosynthesis). Reaction mechanisms have been identified by the use of infrared spectroscopy, transient reaction techniques, and ¹³C and ¹⁸O isotope labeling. Isosynthesis is characterized by two competing

growth steps, CO insertion and condensation between methoxide and enolates. Surface oxygen anion vacancies have been identified as the active site for CO activation by various adsorptive and reactive titrants. Current work is focused on alkali hydroxide/, Al_2O_3 /, Sc_2O_3 /, Y_2O_3 /, and $\text{La}_2\text{O}_3/\text{ZrO}_2$ systems. These systems were selected because acidity, basicity, oxygen anion vacancy concentration, and oxide overlayer effects can be systematically altered. X-ray diffraction, XPS, BET, and gravimetric acid/base titration are used to characterize the catalysts. Conversion of CO to methanol, 2-alcohol dehydration, and labeling studies, which establish the relative rates of CO insertion versus condensation, are used to probe the catalytic properties of these systems.

329. *Morphological Aspects of Surface Reactions*

J.M. White **\$120,000**
Department of Chemistry

The chemical activities of metal single crystals, oxide-supported small metal particles derived from organometallic precursors, and metal thin films on oxide and metal substrates are under investigation. Thin iron films deposited on W(100) have been investigated and, at the 1 monolayer level, differ distinctly from bulk iron with respect to chemisorption of N_2 , NH_3 , and H_2 . The deposition of $\text{Rh}(\text{allyl})_3$ onto silica, the exchange of allyl with CO, NO, and H_2 , and oxidation of rhodium with O_2 are under study. Future work, focused on rhodium, but not limited to it, will involve kinetic measurements at various pressures from ultrahigh vacuum to one atmosphere, using a range of optical, ion, and electron spectroscopies. The long-range goal is to establish correlations between particle morphology and catalytic activity over a broad range of conditions.

Texas A and M University College Station, Texas 77843

330. *Correlations Between Surface Structure and Catalytic Activity/Selectivity*

D.W. Goodman **\$233,000**
Department of Chemistry **(16 mo.)**

This project involves an investigation of the issues that are keys to understanding the relationship between surface structure and catalytic activity/selectivity. These issues are germane to understanding the origins of the enhanced catalytic properties of mixed-metal catalysts. The principal objectives of this project are: (1) the study of the unique catalytic properties of monolayer and submonolayer metal films of "active" catalytic metals on "inactive" substrates; (2) the investigation of methanation, ethane hydrogenolysis, and cyclohexane dehydrogenation of two-dimensional overlayers with emphasis on the critical ensemble size requirements for each of these key probe reactions; and (3) the simulation of small-particle catalysts using corrugated single crystal surfaces.

331. *Catalysts and Mechanisms in Synthesis Reactions*

J.H. Lunsford **\$141,390**
Department of Chemistry

The objective of this research is to understand the role of surface-generated gas phase radicals in catalytic oxidation reactions with emphasis on the oxidative dimerization of methane. A matrix isolation electron spin resonance (MIESR) system is used to analyze the radicals that are formed on a hot metal oxide

surface and then enter the gas phase. Both qualitative and quantitative studies suggest that the gas phase coupling of methyl radicals provides a major pathway for the formation of ethane from methane. By comparing the rate of radical formation with the rate of C_2 (ethane plus ethylene) formation, it is evident that >40% of the C_2 products are formed via these gas phase radicals. This agreement has been found with both lithium-promoted magnesium oxide and sodium-promoted calcium oxide. The technique currently is being extended to include modified transition metal oxides that are known to be effective oxidation catalysts. It is possible that the methyl radicals are bound more strongly on these oxides, which would enhance the coupling reaction on the surface. A mechanism involving radical coupling also is supported by a comparison of the activation energy for methyl radical formation (~ 26 kcal/mol) and that for C_2 formation (~ 54 kcal/mol). A simple kinetic analysis shows that the latter should be twice as great as the former.

332. *Properties of Lanthanide Oxides as Supports for Transition Metal Catalysts*

M.P. Rosynek **\$76,000**
Department of Chemistry

The objective of this research is to provide an understanding of the manner in which variations in metal precursors and oxidic support materials, particularly lanthanide oxides, influence the reduction behaviors and surface/catalytic properties of dispersed nonnoble Group VIII transition metals. Temperature-programmed reduction (TPR) and x-ray photoelectron spectroscopy (XPS) studies have demonstrated that pre-calcination, metal precursor (nitrate, chloride, and acetate), and support material (SiO_2 , CeO_2 , and La_2O_3) all play important and differing roles in determining the mode of reduction and resulting surface chemical nature of dispersed cobalt, as well as profoundly influencing its catalytic behavior for CO hydrogenation and alkane hydrogenolysis reactions. A second area of investigation involves the influence of support and metal loading level variations on the behavior of dispersed nickel for the multipathway conversion of n-paraffins. Cyclic products are formed by homologation of carbonaceous surface species that are deposited following initial catalyst exposure to the hydrocarbon reactant. In this reaction, unlike the case for CO hydrogenation, the electronic nature and chemical identity of the support appear not to play significant roles in determining selectivity, but variations in both metal dispersion and physical properties of the support have pronounced effects on observed catalytic activities and product distributions.

University of Utah Salt Lake City, Utah 84112

333. *Ligand Intermediates in Metal-Catalyzed Reactions*

J.A. Gladysz **\$96,000**
Department of Chemistry

The project goal is the synthesis and study of homogeneous complexes containing ligand types ($-\text{CHO}$, $=\text{CHOH}$, $-\text{CH}_2\text{OH}$, $\equiv\text{C}$, $=\text{CH}_2$, $\text{H}_2\text{C}=\text{O}$, $-\text{OCHO}$, CO_2 , and so forth) intermediate in C_1/C_2 catalytic reactions. We are seeking a mechanistic understanding of key steps and insight needed for the design of new catalysts. Current studies involve the mechanism of the chemical and electrochemical oxidation of methyl complex ($\eta^5\text{-C}_5\text{H}_5$) $\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_3)$ (1, 4 equiv, CH_3CN) to

ethylene complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{CH}_2)]^+$ (2, 1 equiv), acetonitrile complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NCCH}_3)]^+$ (3 equiv), and CH_4 (2 equiv). Complex 2 forms via methyldene complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(=\text{CH}_2)]^+$. This new methyl ligand activation may be coupled with known reactions to achieve the catalytic conversion of methane to ethylene. Electrochemical experiments establish the intermediacy of cation radical $1^{\cdot+}$ and the rate law $-d[1^{\cdot+}]/dt = 2k[1^{\cdot+}]^2$ ($\Delta H^\ddagger = 0.1$ kcal/mol, $\Delta S^\ddagger = -46$ eu). This suggests an exothermic pre-equilibrium dimerization of $0.1^{\cdot+}$ followed by a subsequent rate determining step. Experiments with deuteromethyl complex 1-d₃ and optically active (+)-(S)-1 give (0°C) $k_H/k_D = 3.0$ (>90% CD₄) and $k_{(+)} / k_{\pm} = 1.6$ (preference for homochiral coupling). We also completed a conformational study of the formyl ligand in $\eta^5\text{-C}_5\text{H}_5\text{Re}(\text{NO})\text{-}(\text{PPh}_3)(\text{CHO})$, and prepared a series of rhenium/main group metal bridging CO₂ complexes $\eta^5\text{-C}_5\text{H}_5\text{Re}(\text{NO})\text{-}(\text{PPh}_3)(\text{CHO}_2\text{ML}_n)$ (M = Li, K, Ge, Sn, Pb). Their properties are under study.

334. Carbon-13 NMR of Solid-State Hydrocarbons and Related Substances
D.M. Grant, R.M. Pugmire **\$103,777**
Department of Chemistry

This project objective is to develop new 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 ¹³C 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 ¹³C 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. The nine ¹³C CSA tensors in 1,3,5-trimethoxybenzene (1,3,5-TMB) were measured and compared with previous one-dimensional results. Chemical shift values of all carbons in 1,3,5-TMB, 1,2,3-TMB, and 1,4-DMB, and the orientation of their principle axes were determined. *Ab initio* calculations of the shielding tensors were performed. Results agreed with experimental substituent effects obtained from correlating values obtained in the polysubstituted compounds. Carbon-13 NMR shielding tensors were determined for two anthracite coals and a fusinite maceral, using powder pattern line-shapes; theoretical calculations on the model compound circumcoronene(1) supported these interpretations. Spectroscopic analysis of nonprotonated to protonated aromatic carbons agreed with elemental analysis and dipolar dephasing NMR techniques. The method is 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.

Wayne State University
Detroit, Michigan 48202

335. Surface Composition-Reactivity Relationships in Heterogeneous Catalysis
A. Brenner **\$98,000**
Department of Chemistry

Research has focused on understanding the differences in activity between homogeneous and heterogeneous catalysts. Limited data from the literature show that the rates of H₂-D₂ exchange over homogeneous hydrogenation catalysts are much lower than the rates over metal surfaces. In addition, ethylene deuteration over homogeneous catalysts and metal oxides usually gives nearly 100% d₂-ethane, whereas over metal surfaces there is a broad smear of deuterated ethanes. The differences in reactivity are related to the fact that metal surfaces have many interacting sites whereas on the other catalysts the sites are usually noninteracting. These two reactions are being used as probes of the nature of catalytic sites, a technique termed "reactive characterization." The rate of H₂-D₂ exchange was measured over a variety of metals. The activities per surface metal atom are in the order Ru>Rh>Fe>Ir>Pd>Mo>Os>Pt≈W>Ni>Co>>Cu≈Ag≈Au. Similar measurements are currently under way for several homogeneous catalysts to better define the differences in rates. Ethylene deuteration over molybdenum metal gives a broad smear of products, but over MoO₂ mainly d₂-ethane is obtained. This indicates that this reaction is a useful probe of the nature of the active sites. The technique of reactive characterization is also being applied to highly dispersed catalysts of supported metals to see if the metal is primarily atomically isolated or has agglomerated.

University of Wisconsin
Madison, Wisconsin 53706

336. Organometallic Chemistry of Bimetallic Compounds
C.P. Casey **\$108,000**
Department of Chemistry

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 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 reactions of new zirconium-ruthenium and zirconium-rhenium compounds that possess highly polar metal-metal bonds are being studied.

**337. Experimental and Kinetic Modeling of Acid/
Base and Redox Reactions over Oxide Catalysts**
J.A. Dumescic **\$89,000**
Department of Chemical Engineering

Microcalorimetric studies have been conducted to establish a thermodynamic scale of acid strength for the following series of Lewis acid sites on silica: gallium, aluminum, zinc, iron, scandium, and magnesium. It was found that the acid strength could be correlated with the Sanderson electronegativity of the metal oxide, thereby providing a predictive means of preparing Lewis acid catalysts with desired strength. During the past year studies of the generation of Bronsted acid sites by doping metal cations onto silica have been initiated. The formation of pyridinium cations (as detected by infrared spectroscopy) has been used as the criterion for Bronsted acidity. Bronsted sites have been found to be generated by aluminum, gallium, scandium, vanadium, and molybdenum on silica, whereas iron, zinc, and magnesium generate only Lewis acid sites. Pauling's electrostatic bond strength is a useful concept to rationalize these results. It appears that a Bronsted acid site is formed when the sum of the electrostatic bond strengths of cations surrounding a surface oxygen anion is between 1.9 and 1.6 valence units. Isopropanol dehydration studies over all silica-supported samples indicate that Bronsted acid sites are more effective catalytic centers than are Lewis acid sites for this reaction. Current studies deal with the formulation of a thermodynamic scale of Bronsted acidity on surfaces.

Yale University
New Haven, Connecticut 06520

**338. Studies in Carbon-Carbon Bond Activation/
Alkane Photoreactions with Mercury Vapor**
R.H. Crabtree **\$133,300**
Department of Chemistry **(16 mo.)**

Current research has now moved entirely into the area of mercury vapor photosensitized catalysis. The most exciting results involve CH₄. Methane has been directly converted to methanol with N₂O, Hg, and light. Methane/air gives CH₃OOH, and methane/methanol gives CH₃CH₂OH. Initial work on the higher alkanes shows that propane conversion is especially efficient. Patent protection has been obtained, and a corporation is pursuing related commercial applications of this work. Other substrates under investigation include alcohols, ethers, amines, silanes, and fluorocarbons. Mechanistic studies show that free radicals are the kinetically important intermediates in the catalytic scheme. Future studies will extend the work by trapping these radicals in other synthetically useful ways.

**339. A Spectroscopic and Catalytic Investigation of
Active Phase-Support Interactions**
G.L. Haller **\$96,000**
Department of Chemical Engineering

Coinpregnation of copper and ruthenium on Cab-O-Sil HS5 decreases the hydrogen uptake by the reduced catalyst below the amount taken up by a sample containing ruthenium only. On many other silicas, represented here by Cab-O-Sil M5, the presence of copper suppresses catalytic activity for hydrogenolysis reactions but increases the hydrogen uptake. It was shown that the increased gas uptake is not caused solely by spillover since CO uptake also increases for the latter class of catalysts. Rather, the discrepant behavior is correlated with differences in

the environment of the copper (seen in x-ray absorption and EPR spectra). Differences develop in the drying step during catalyst preparation and likely involve surface hydroxyl groups since dehydroxylation of the silicas tends to diminish differences in catalytic activity and in the infrared spectra of adsorbed CO.

**340. The Role of d-Electrons in Chemisorption and
Metal-Support Interactions Studied by Electron
Spectroscopy**
V. Henrich **\$96,500**
Section of Applied Physics **(15 mo.)**

The goal of this research project is to understand the various effects that contribute to the strong metal-support interactions (SMSI) that occur when small metal catalyst particles are supported on reducible transition-metal oxides, by using model catalysts fabricated on well-characterized single-crystal supports. Most attention has been directed at the Rh/TiO₂ (110) system, where electron spectroscopic techniques such as photoemission, Auger, and energy-loss spectroscopies have provided unambiguous evidence for (1) physical encapsulation (decoration) of the catalyst particles by TiO_x suboxide moieties after high-temperature reduction and (2) electron charge transfer from reduced cations in the support to the catalyst metal atoms. The latter effect occurs even if the surface is reduced by inert gas ion bombardment rather than high-temperature reduction. However, only the former effect is found to contribute to the suppression of CO chemisorption that is characteristic of SMSI. Studies of the electronic properties of model vanadia surfaces prepared by various techniques contribute an initial step toward extending this Rh/TiO₂ work to vanadia-based catalysts.

341. Energies of Organic Compounds
K.B. Wiberg **\$102,000**
Department of Chemistry

This research project is designed to provide information on the energies and conformations of organic molecules via reaction calorimetry and theoretical calculations, and to use these data to improve empirical and semiempirical schemes (e.g., molecular mechanics) for estimating the properties of organic compounds. A major effort has been made to develop a method for determining heats of reduction of carbonyl compounds, and it has successfully been used to study aldehydes, ketones, esters, and lactones. The results have led to significant revisions of some of the literature values for these compounds. The measurement of heats of hydration of alkenes has provided new information on tertiary alcohols. Theoretical calculations of rotational barriers have given information as to their source as well as the potential functions needed for molecular modeling.

Separations and Analysis

Aerospace Corporation Los Angeles, California 90009

342. *Isotopically Selective, Two-Step, Laser Photodissociation of Triatomic Molecules in Cryogenic Solutions*

P.F. Zittel \$131,000
Chemistry and Physics Laboratory

This research is directed toward understanding photophysical, energy transfer, and chemical reaction processes relevant to isotope separation by two-step laser photodissociation of small molecules in cryogenic solution. The two-step technique involves the excitation of molecules containing a chosen atomic isotope to an excited vibrational state by an infrared laser, followed by ultraviolet laser photodissociation and chemical scavenging of the photofragments. Focus is on photodissociation of OCS dissolved in liquid rare gases. Oxygen isotopes have recently been enriched by a factor of four using this technique. The dependence of isotope enrichment on experimental variables (e.g., laser intensity, timing, and sample composition) is used to probe vibrational relaxation and chemical reaction processes in the cryogenic solution. A vibration-to-translation relaxation time of 1.3 microseconds has been determined for relaxation of OCS by liquid argon at 84 K. The cryogenic solution work is complemented by gas phase experiments designed to measure cross sections for photodissociation of molecules in specific excited vibrational states. Of increasing interest are photodissociation cross sections and vibrational relaxation rates for highly excited vibrational states of small molecules in both the gas phase and in cryogenic solution.

Auburn University Auburn, Alabama 36849

343. *Interfacial Chemistry in Solvent Extraction Systems*

R.D. Neuman \$102,000
Department of Chemical Engineering

Significant questions remain to be resolved pertaining to the interfacial chemistry in the solvent extraction of metal ions in hydrometallurgical and nuclear industries. Studies of liquid/liquid interfaces, however, are very difficult and are crucial to developing new or improved processing technologies. This research emphasizes characterization of the liquid/liquid interface in organophosphorus solvent extraction systems associated with Zn^{2+} , Co^{2+} , Ni^{2+} , and UO_2^{2+} . Recent advances in laser and spectroscopic techniques provide novel tools for investigating interfacial films from a microscopic point of view. For example, studies with a Brooks' frame for manipulating model extractant films at the liquid/liquid interface in conjunction with laser light scattering, steady-state and time-dependent fluorescence, second harmonic generation, and FT-IR techniques will provide information about the dynamic properties and the structural organization of extractant molecules in the interfacial zone. In addition, the nature of the microenvironment about the polar head groups of extractant films is being investigated using laser fluorescence techniques. The structure of microscopic interfaces (e.g., reversed micelles and microemulsion droplets) that can form in these extraction systems will

also be examined using SANS to answer questions concerning their physicochemical nature.

Brigham Young University Provo, Utah 84602

344. *Novel Macrocyclic Carriers for Proton-Coupled Liquid Membrane Transport*

J.D. Lamb \$81,710
Department of Chemistry

The macrocycle-mediated metal cation transport in hydrophobic liquid membrane systems is investigated. Potential macrocyclic carriers are screened by measuring extraction equilibrium constants and partition coefficients. Macrocycles of particular interest are then studied in the potentially practical emulsion and hollow fiber supported liquid membrane systems. A two-module hollow fiber system is of particular 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 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, Rhode Island 02912

345. *Photochemical Generation of the Optoacoustic Effect*

G.J. Diebold \$80,000
Department of Chemistry

Current research is concerned with investigating a new technique of generating the optoacoustic effect through spatial modulation of light beams where the beam size is modulated but its total power is kept constant. The wavelength of the light is such that radicals are created by the absorption of the radiation. The presence of a nonlinear recombination mechanism for the radicals causes an optoacoustic effect to be generated. Because of the presence of diffusion, the magnitude of the effect varies as a function of the spot size; this dependence will permit the determination of diffusion coefficients for radicals. This method is general and can be used with other detection methods (such as electron spin resonance or optical absorption) and applied to different chemical systems. Other experiments will be done to demonstrate a new technique of selective isotope ionization. A two-photon interference effect dependent on laser polarization will be investigated to determine the degree of suppression of the ionization signal from a major isotopic constituent relative to a minor one. The interference technique can be used in conjunction with existing spectroscopic techniques based on isotope shifts.

University of California
Los Angeles, California 90024

346. Multiheteromacrocycles That Complex Metal Ions
D.J. Cram **\$125,000**
Department of Chemistry and Biochemistry

The goals of this research are to design, synthesize, and test organic multiheteromacrocycles for their abilities to complex metal anions and inorganic cations. The liganding systems are highly preorganized for binding during their synthesis rather than during their complexing acts (principle of preorganization). Most of the functional groups of organic chemistry are being tested as ligating sites. Ion specificity in binding of Li^+ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ is a special goal that makes use of stereoelectronic complementarity between host and guest (principle of complementarity). Systems that simultaneously bind and lipophilize both anions and cations of salts are of particular interest. Correlations between host-guest structures, binding free energies, rates of complexation-decomplexation, and solvation effects are general goals of this research.

Columbia University
New York, New York 10027

347. Utilization of Magnetic Effects as a Means of Isotope Enrichment
N.J. Turro **\$80,685**
Department of Chemistry

The major objective of this research has been the use of the magnetic isotope effect to optimize the separation of isotopes based on differences in magnetic properties rather than mass properties. To achieve this objective, a model system, the photolysis of ketones, has been developed to examine the influence of systematic variation of experimental parameters on the efficiency of isotope separation by the magnetic isotope effect. The separation of ^{13}C has been studied in detail. Variables influencing the efficiency of the separation (e.g., external magnetic fields, temperature, ketone structure, environmental structure, and viscosity) have been examined. From these results, a model involving a key intermediate, the radical pair (or biradical), has been found to be generally involved and to be the critical intellectual unit that determines the mechanistic protocol that drives experiments. Current research is directed toward investigating the role of microheterogeneous environments and multiphoton optical excitation on the efficiency of separation. Future research will involve the use of radio frequency and microwave frequency to enhance the separation efficiency.

University of Delaware
Newark, Delaware 19716

348. Studies of the Analyte-Carrier Interface in Multicomponent Flow Injection Analysis
S.D. Brown **\$67,000**
Department of Chemistry

Separation by a physical or chemical step is the most common route to analysis of complex samples. However, separation steps are difficult to optimize and are highly matrix dependent. Thus, it is of considerable interest to examine novel methods for the analysis of complex mixtures, such as ones based on competitive

kinetic assay, or on mathematical methods for resolution of cointerfering responses. This project involves the study of digital filters developed for kinetic analysis of materials in flowing media and filters for enhancing the resolution of transient responses, such as those found in kinetic analysis, flow injection analysis, and liquid chromatographic separations. The goal is a better understanding of the effect of homogeneous and heterogeneous chemical reactions for accomplishing sufficient separation of mixtures to permit their characterization.

Duke University
Durham, North Carolina 27706

349. Studies of Multifrequency Phase-Resolved Fluorescence Spectroscopy for Spectral Fingerprinting
L.B. McGown **\$80,000**
Department of Chemistry **(18 mo.)**

The purpose of this project is to study the use of phase-resolved fluorescence spectroscopy (PRFS) for the fingerprinting of real, complex samples. The PRFS fingerprint contains fluorescence spectral and lifetime information, which can be used to study the nature of the sample in terms of both composition and dynamic, intermolecular interactions (aggregation, quenching, energy transfer, and so forth). Multifrequency PRFS instrumentation will allow the collection of PRFS fingerprints at a series of modulation frequencies in order to selectively view fluorescence signals within a given lifetime range in each fingerprint. An important component of the research is the use of sodium taurocholate (NaTC) micelles to isolate fluorescent molecules in aqueous solution, thereby minimizing the dynamic interactions. Comparison of the PRFS fingerprints for a sample in NaTC and in simple solvents will provide information about (1) the role of dynamic interactions in determining the fingerprint characteristics and (2) the nature of the sample itself.

University of Florida
Gainesville, Florida 32611

350. Development of Laser-Excited Atomic Fluorescence and Ionization Spectrometric Methods
J.D. Winefordner **\$100,000**
Department of Chemistry **(8 mo.)**

Laser excited atomic spectrometric methods will be investigated in order to achieve high selectivity and detection power. The techniques to be studied involve laser-enhanced ionization in flames and furnaces, laser-enhanced fluorescence in flames, plasmas and furnaces, and double resonance fluorescence in flames and plasmas for nonmetals. The techniques will be used for both diagnostical measurements of species in flames, plasmas, and furnaces as well as for analytical measurements. The emphasis will be 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 diagnostical studies will be directed towards (1) a more thorough understanding of the mechanism of atomization, ionization, and dissociation of analyte species in plasmas and furnaces; and (2) the optimization of experimental conditions to obtain the best analytical results.

George Washington University
Washington, District of Columbia 20052

351. *New High-Temperature Plasmas and Sample Introduction Systems for Analytical Atomic Emission Spectrometry*
A. Montaser **\$67,000**
Department of Chemistry

New high-temperature plasmas and new sample introduction systems are investigated for rapid elemental analysis of gases, solutions, and solids using atomic emission spectrometry and mass spectrometry. These devices offer promise of solving analytical problems in the fields of energy generation, environmental pollution, biomedicine, and nutrition. Emphasis is on: (1) generation and fundamental investigation of annular helium plasmas that are suitable for the excitation of high-energy spectral lines, to enhance the detecting powers of a number of elements; (2) generation of plasmas that require low gas flows and low input power, to decrease the cost of analytical determination; (3) formation and investigation of tandem plasmas to separate and maximize atomization and excitation processes; and (4) development and characterization of new sample introduction systems that consume microliter or microgram quantities of samples. Investigations include 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, Georgia 30332

352. *Fundamental Studies with a Monodisperse Aerosol-Based Liquid Chromatography/Mass Spectrometry Interface (MAGIC-LC/MS)*
R.F. Browner **\$90,000**
School of Chemistry (15 mo.)

The investigation of a monodispersed aerosol generation interface for liquid chromatography/mass spectrometry (MAGIC-LC/MS) has continued. A number of instrumental developments to the interface have been accomplished, based on the need to improve chromatographic performance using the interface. The improved interface has been thoroughly characterized for the purpose of determining the quality of the chromatographic performance. This work has demonstrated that the interface is capable of producing separations that have comparable, or superior peak broadening to conventional ultraviolet detectors for liquid chromatography. The scope of the interface has been further studied for important classes of compounds, including high molecular weight polynuclear aromatic compounds. Searchable quality electron impact spectra for compounds with molecular weights in excess of 550 daltons (e.g. rubrene) have been readily produced. The transport properties of the interface have been thoroughly studied using a specially constructed test device, to correlate the signals observed in the mass spectrometer with the transport properties of the interface.

Hampton University
Hampton, Virginia 23668

353. *Use of Ion Chromatography-D.C. Plasma Atomic Emission Spectroscopy for the Speciation of Trace Metals*
I.T. Urasa **\$50,000**
Department of Chemistry

The project objectives are (1) to study the factors that influence the use of d.c. plasma atomic emission spectrometry (DCPAES) as an element-specific detection method (ESD) for ion chromatography (IC); and (2) to tailor the combined analytical system to speciation of trace elements. The use of ESD has the following advantages: (1) response of the detector to a specific element can lead to an improved chromatographic analysis, especially when only partial separation of the mixture components is achieved; (2) measurement sensitivity can be improved; and (3) interference and matrix effects can be eliminated. This detection approach has an added advantage in multielement measurement capability suitable for determining metals and nonmetals. In this research the system is being evaluated as a detector for IC effluents consisting of selected species of arsenic, chromium, iron, manganese, nickel, and vanadium. The fundamental hypothesis is that DCPAES can serve as a sensitive ESD for IC allowing the separation and detection of a variety of species of elements and in monitoring the transformations that these elements may undergo as a result of chemical and/or biological changes. Various measures can be used with this detector to improve measurement sensitivity. These are also being studied.

University of Houston
Houston, Texas 77004

354. *Mechanisms of Thickening, Cake Filtration, Centrifugation, and Expression*
F.M. Tiller **\$140,000**
Department of Chemical Engineering (17 mo.)

Fluid-particle separation is being studied both theoretically and experimentally. Of primary interest is the unification of the theory underlying sedimentation, thickening, filtration, centrifugation, deliquoring, and washing. Common to these operations is the compaction of particulate structures under loads derived from fluid friction, gravity, centrifugal forces, mechanically applied stresses, and diffusion. Generalized simultaneous differential equations governing fluid flow, deformation of particulate structures, and particle deposition form the foundation for attacking various classes of problems. An experimental correlation of permeability and compactibility in relation to colloidal and rheological properties is under way. Continuum laws involving sedimentation and flow through porous media are being examined from theoretical and experimental standpoints. Examination of data involving stress distribution in particulate matrices, local deviations in concentration of sedimenting suspensions using a computerized axial tomographic scanner (CATSCAN), and microscopic examination of beds of particles indicates that revision of some commonly accepted concepts may be required. Theoretical equations have been developed to describe both radial and planar deposition of ceramic suspensions in slip casting.

University of Idaho
Moscow, Idaho 83843

- 355. *The Effect of Electric Fields on Liquid Extraction***
T.E. Carleson **\$49,777**
Department of Chemical Engineering

A parallel 4 kV/cm, dc field imposed upon single, conductive drops forming in a dielectric continuous phase was found to decrease drop size by 40% and increase terminal velocities by 25%, mass-transfer coefficients by 50%, and the extraction efficiencies by 50%. The observed effects of the field were roughly correlated ($\pm 40\%$) with a simple model based upon a force balance upon the forming and falling drops. A predicted mass-transfer coefficient for an uncharged, oscillating drop of the same size and at the same velocity as the charged drop agreed to within 30% of that calculated from the experiments. The effects of the field and drop charge upon the mass-transfer process appear to be mainly caused by the increased drop surface area/volume ratio produced by the field. Similar experimental work with a charged plate, three stage sieve tray extraction column showed an increase in extraction efficiency of 20% and an increased throughput of 30% in the presence of a 2 kV/cm applied field. These results are being compared to those predicted by standard mass-transfer correlations for uncharged drops. Additional work with a charged liquid interface indicates that electrical charge inhibits the interfacial turbulence induced by the effect of concentration gradients on interfacial tension.

University of Illinois
Urbana, Illinois 61801

- 356. *Thin Films Under Chemical Stress***
P.W. Bohn **\$130,000**
Department of Chemistry (15 mo.)

This work is to study the means by which chemical analysis of thin films of nonuniform composition can be conducted using techniques of optical spectroscopy that are potentially capable of providing spatially resolved concentration profiles. Research is directed at improving techniques for monitoring the distribution of chemical reagents used to selectively treat polymer films (e.g., in the development of exposed photoresists for semiconductor fabrication). Such processes can be operated more efficiently if the local reagent concentrations are monitored directly.

- 357. *Theta Pinch Discharges for Emission Spectrochemical Analysis***
A. Scheeline **\$75,000**
Department of Chemistry

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. Quantitative measurements of emission from selected single elements with respect to a major constituent are now being made to determine the reproducibility and accuracy of vaporization. Optimization with respect to measurement time, spatial position, discharge pressure, and source electrical properties is being concurrently performed. Variation in sample uptake because of modification of the ceramic by successive discharges

is also being studied, both as the variation affects analysis and also with a view to learning how material properties change with shock heating to very high temperatures. Use of an echelle spectrometer and charge-coupled array detector to allow single shot multielement analysis is planned. Design of the spectrometer is currently under way.

Kansas State University
Manhattan, Kansas 66506

- 358. *Development of a Novel Hadamard Transform Infrared Spectrometer for Analytical Chemistry***
W.G. Fateley **\$85,000**
Department of Chemistry

LC-SIM Hadamard transform spectrometry has been achieved as a simultaneous multiwavelength detection system for Raman spectroscopy. Multiplexed Raman data are obtained using an Ar⁺ laser lasing at 514.5 nm and a room temperature silicon photodiode. A conventional 90° scattering geometry is used for measurements. It is demonstrated that the LC-SIM Hadamard transform spectrometer with Ar⁺ laser possesses the capability to perform spectral subtraction, the ability to obtain depolarization ratios of Raman bands, and to function as a selectively tunable optical filter for both Rayleigh line rejection and optical band notching. It is also demonstrated that for the Hadamard transform Raman experiment, the silicon photodiode as detector produced spectra with slightly better signal-to-noise ratios than the photomultiplier tube (PMT) as detector, although the PMT shows an increase in sensitivity. The next experiments will involve the Nd:Yag 1.06 μ exciting frequency. In addition, emission studies of elements have been quite successful.

Lehigh University
Bethlehem, Pennsylvania 18015

- 359. *Perforated Monolayers***
S.L. Regen **\$65,000**
Department of Chemistry

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.

University of Maryland
College Park, Maryland 20742

- 360. *Studies of Highly Selective Sorptive Effects with Application to Paraffins and Petroporphyrins***
D.H. Freeman **\$63,000**
Department of Chemistry

Geochemistry is challenged by a variety of problems, including a pervasive need for improved chemical analysis. The measurement of organic chemicals in minerals is perturbed by chemical interferences, extraction and separation difficulties, and

sample-to-sample variations. Problems are being solved through an interest in geoporphyrins. These persistent chemical descendants of chlorophyll possess structural and isotopic properties that are of increasing importance to the study of geology. The existing analytical procedures are slow and unreliable, chiefly because the geoporphyrins are relatively large molecules that are only marginally volatile and thus inappropriate for gas chromatography. Discovery and use of chromatographic deasphaltation has led to the development of speedier procedures, and a start has been made toward statistical control of the analysis. In addition, geoporphyrin assay by visible light spectrophotometry is being improved by the use of derivative spectroscopy. However, the accuracy remains unknown because of inadequate standards. The limits of the available standards are being mapped to search for improved ways to measure geochemical compounds whose structures and properties are only partly known. Even more stringent chemical isolations of geoporphyrins are being developed as a possible way to isolate standards and for isotopic mass spectrometry.

University of Minnesota
Minneapolis, Minnesota 55455

361. *Continuous Reaction Chromatography*
R. Aris, R.W. Carr **\$78,000**
Department of Chemical Engineering and Materials Science

The combination of the separative effect of chromatography and the generative effect of chemical reaction is being systematically investigated. Past work includes the use of a rotating annulus for liquid-phase reaction on a solid adsorbent and gas-phase reaction on a solid catalyst. A theoretical analysis of the countercurrent moving bed showed how thermodynamic limitations of a fixed bed could be overcome, and an experimental countercurrent reactor was successfully built and tested. Current emphasis is on the switched bed in which countercurrency is simulated in a discontinuous fashion by switching the feed point between short fixed beds in a cyclic manner. It has been shown that this gives better performance than a single fixed bed and can emulate the countercurrent system. A small switched column has been built and tested on separations and is now running as a reactor. Simplified computational methods for difficult separations are also being investigated.

University of Missouri
Rolla, Missouri 65401

362. *Use of Functionalized Surfactants and Cyclodextrins in Chemical Analysis*
D.W. Armstrong **\$73,000**
Department of Chemistry

Organizing media such as micelles, microemulsions, vesicles, cyclodextrins, and so forth are playing an increasingly important role in chemical analysis. New separation and spectroscopic detection methods have been developed using highly specific micelles, microemulsions, and cyclodextrins. For example, micelles composed of brominated Brij 96 surfactant allow resonance Raman spectra to be taken of low levels of many fluorescent molecules. This is possible because this micelle shifts absorption and luminescence bands, changes luminescence lifetimes and quantum yields, facilitates quenching effects, allows

the use of aqueous rather than organic solutions, stabilizes transient species, alters fluorescence depolarization, and changes the apparent pKa of ionizable solutes. Good resonance Raman spectra were obtained for fluorescent metalloporphyrins using the micellar approach. A variety of fluorescent, heterocyclic-aromatic compounds were successfully analyzed using ultraviolet laser excitation. The potential use of this technique as a detection method for micelles liquid chromatography is being investigated. A particularly novel use of micelles and microemulsions is in field flow fractionation (FFF). It has been demonstrated that the molecular weight range of FFF can be extended by several orders of magnitude by use of secondary equilibrium to these species. This allowed the first separation of small solutes by FFF. The theory, mechanism, and application of this technique are being explored in detail. It appears that FFF will be an effective method for characterizing the size and aggregation number of association colloids.

National Bureau of Standards
Gaithersburg, Maryland 20899

363. *Competitive Ion Kinetics in Direct Mass Spectrometric Organic Speciation*
L.W. Sieck **\$138,000**
Center for Chemical Physics

This project involves the measurement of fundamental properties of gas phase ions. The project uses the NBS pulsed electron beam mass spectrometer as the prime experimental facility, and an ICR instrument and triple MS system are also available. Emphasis is in two areas. One area is definition of the thermochemistry of anionic association and cluster ions via variable-temperature equilibrium measurements. Correlation lines, which express the dependence of the bond strengths upon the differences between the acidities of the two interacting partners, are then developed for predictive purposes for various classes of ligands and anions. The temperature dependence of various particle transfer reactions is also under investigation. The most extensive aspect of this project involves measurement of proton transfer equilibria of the type $A^- + BH \leftrightarrow B^- + AH$ as a function of temperature in order to accurately define the acidity difference between A and B. Interlocking ladders of relative ΔH and ΔS are then referenced to primary standards such as H_2O , HCN, HCl, and so forth, in order to provide an absolute gas phase acidity scale. Other studies include the pyrolysis of protonated mercaptans and particle transfer reactions in SF_6 -additive mixtures.

State University of New York/Stony Brook
Stony Brook, New York 11794

364. *Stable Isotope Studies*
T. Ishida **\$92,100**
Department of Chemistry

With a general goal of developing new stable isotope fractionation processes and investigating the related fields of molecular force studies and isotope effects, three areas are explored. One area is the development of a new type of hydrophobic catalyst for the hydrogen isotope exchange between dihydrogen and liquid water, which will basically consist of polycrystalline platinum aggregates and a chemically modified flow-through electrode, the latter also acting as an exchange column packing. The

study includes correlations between the surface structure of chemically modified electrodes, the hydrophobicity, and the catalytic activities. It has been established that an *in situ* regeneration of the catalytic surfaces is possible. The second area concerns theoretical correlations between the vibrational zero-point energy (ZPE) and molecular structures, and correlations between the intermolecular forces and the shifts in ZPE caused by isotope substitutions and phase changes. Studies of molecular structure and ZPE-shifts caused by hydrogen/deuterium substitutions have been recently completed. The third area includes studies of liquid ammonia systems, for understanding intermolecular interactions between ammonia molecules in the liquid and those between ammonia molecules and dissolved lithium metal, for a possible application in the lithium isotope separation. A molecular dynamics study of lithium ion in liquid ammonia has recently been completed.

University of North Carolina
Chapel Hill, North Carolina 27514

365. *Solid-State Voltammetry and Sensors in Gases and Other Nonionic Media*
R.W. Murray \$75,000
Department of Chemistry

Miniaturized electrochemical cells suitable for transient electrochemical voltammetry of electroactive materials dissolved in or affixed to thin ionically conducting polymer films have been designed and tested. The cells contain microdisk electrodes sealed in glass capillaries or are fashioned as microband electrodes microlithographically. Present experiments have two thrusts. First, a range of electrochemical methodologies, with appropriate boundary value theory, is being developed that can be applied to electrochemistry with rigid polymeric solvents. As much as possible of the diagnostic power developed for electrochemical voltammetry in fluid electrolytes will be brought to rigid media experiments. 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 can form the basis for basic investigation of polymer plasticization effects and chemical reactivity inside polymeric phases, and may be applied to design sensors for bathing gas constituents.

University of Oklahoma
Norman, Oklahoma 73019

366. *A Study of Micellar-Enhanced Ultrafiltration*
J.F. Scamehorn, \$67,000
S.D. Christian
School of Chemical Engineering and Materials Science

In micellar-enhanced ultrafiltration (MEUF), surfactant is added to an aqueous stream containing dissolved organic and/or multivalent ions. The micelles (aggregates containing approximately 100 molecules) formed by the surfactants tend to solubilize the organics and bind the multivalent ions if the surfactant is of opposite charge to these ions. The solution is treated using ultrafiltration with membrane pore sizes small enough to block the passage of the micelles. Extremely pure permeate streams have been produced using MEUF from feed streams containing

both organics and heavy metals (rejections of 99.8%). Divalent cationic ions (with anionic surfactant) and divalent anionic ions (with cationic surfactant) have been shown to be removed with approximately the same efficiency, consistent with an electrostatic mechanism of binding to the micelles. The ability of MEUF to remove organic solute or multivalent ions is approximately the same, whether or not both types of species are present. Recent work has shown that reasonable efficiencies of removal are attainable at low surfactant concentrations because of the contribution of the gel layer to the separation.

Oklahoma State University
Stillwater, Oklahoma 74078-0447

367. *Unsegmented Continuous Flow Sample Processing and Electrochemical Detection and Determination of Gaseous Species*
H.A. Mottola \$70,000
Department of Chemistry

This work investigates a new family of chemically modified electrodes based on the redox characteristics of the iron(II)/iron(III) complexes with 1,10-phenanthroline and related ligands. Three basic ways of producing modified surfaces are being critically studied: (1) direct admixing of relatively insoluble salts (in aqueous media) of a complex cation with carbon pastes, (2) covalent binding of the complex cation to chemically modified graphite and pasting liquids, and (3) oxidative electropolymerization of some derivative complex cation of the same family of ligands. The electrochemical performance of the modified surfaces is characterized by cyclic voltammetry and chronocoulometry. The prepared, modified surfaces are then incorporated into different configurations of electrochemical sensors for detection/determination of redox species in continuous-flow systems. The sensors are evaluated for their hydrodynamic electrochemical behavior as amperometric and coulometric detectors. Target analytes in these studies are gaseous redox species (e.g., NO_x, O₃, SO₂, H₂S).

Purdue University
West Lafayette, Indiana 47907

368. *Reactions of Gaseous Metal Ions/Their Clusters in the Gas Phase Using Laser Ionization: Ion Cyclotron Resonance Spectroscopy*
B.S. Freiser \$160,000
Department of Chemistry (18 mo.)

Studies on the gas phase chemistry and photochemistry of bare atomic metal ions, metal ion complexes, and small metal cluster ions continue. These studies use a methodology involving laser desorption: Fourier transform mass spectrometry. One of the most exciting and fruitful areas of this research has been photodissociation of these species. Two of the major findings from this work are (1) transition metal ion-containing species in general have measurable photodissociation cross sections and (2) photodissociation thresholds are often thermodynamically determined and can yield absolute bond energies. The preliminary studies have encompassed three general categories of metal containing ions, ML⁺, ML₂⁺, and MFe⁺ (M = metal; L = ligand), and have yielded a good deal of thermodynamic, structural, and mechanistic information. Study of the effects of internal energy on the reaction kinetics of ML⁺ species, and the

chemistry of multiply charged ions has also begun. LaFe^{2+} , which is stable to spontaneous dissociation, has been synthesized and studied. Further theoretical and experimental work is under way to understand the bonding in this unusual type of species.

Rensselaer Polytechnic Institute Troy, New York 12180

369. *Macrocyclic Ligands for Uranium Complexation* K.T. Potts **\$95,000** Department of Chemistry

Several macrocycles have been prepared as potential complexation agents for the uranyl ion. Containing oligoacylureas and oligobiurets as the ligating system, these macrocycles were designed using a computer-aided-design approach. Control of the cavity diameter was exerted by variation of the peripheral constituents of the macrocycles, and energy minimizations and docking of the guest uranyl ion were utilized in these modeling studies. Preliminary studies indicate that these macrocycles form stable complexes with the uranyl ion. Novel isocyanate chemistry has been developed to prepare a wide variety of bis(ethoxycarbonylureas and thioureas) and related precursors. An open-chain uranophilic ligand was found to form a ready 1:1 complex with the uranyl ion. On dissolution in DMSO, this complex underwent an extremely interesting rearrangement to form a 2:1 uranyl ion-ligand complex. The structures of these complexes were established by a variety of analytical techniques as well as by single-crystal x-ray data.

San Diego State University San Diego, California 92182

370. *Synthesis and Characterization of Mesomorphic and Other Stationary Phases* R.J. Laub **\$77,000** Department of Chemistry

This work is concerned with studies of the synthesis and physicochemical characterization of mesomorphic side-chain (liquid-crystalline) and other stationary phases that offer unprecedented selectivity in the chromatographic separation and analysis of complex organic mixtures. The first portion of the work is devoted to the synthesis of mesomorphic polysiloxane (MEPSIL) solvents that yield crystalline-to-nematic transition temperatures of less than ambient; and nematic-to-isotropic transitions that approach 350°C. Characterization of the phases is being conducted in terms of the measurement and interpretation of probe-solute specific retention volumes, activity coefficients, and interaction parameters. The variation of retentions as functions of the depth and method of immobilization of stationary-phase films is also being evaluated. Certain smectic MEPSILs are being synthesized, and direct comparisons will be made of their physicochemical and chromatographic properties with the most useful of the nematic MEPSILs. Finally, several mesomorphic phases with a polyacrylate backbone (MEPCRYLs) will be synthesized and characterized; and their utility as GC stationary liquids will be contrasted with the smectic and nematic MEPSIL solvents fabricated in earlier portions of the work.

Syracuse University Syracuse, New York 13244

371. *Mechanisms of Gas Permeation Through Polymer Membranes* S.A. Stern **\$86,000** Department of Chemical Engineering and Materials Science

Permeability, diffusion, and solubility coefficients for gases in many glassy polymer membranes are strongly nonlinear functions of penetrant gas pressure (or concentration in the polymers). This behavior can be described quantitatively in terms of a "dual-mode sorption" (DMS) model, which postulates that a metastable excess free volume is localized in some domains of glassy polymers (Langmuir domains). It was previously found that the solution and transport of CH_4 , C_2H_6 , $n\text{-C}_4\text{H}_{10}$, and CO_2 in poly(*n*-butyl methacrylate)(PnBMA) did not exhibit DMS effects even 40°C below the glass-transition temperature of the polymer ($T_g = 27$ to 35°C). The absence of such effects was attributed to the fact that the excess free volume in PnBMA was very small. However, it was predicted that DMS effects should appear at much lower temperatures, because the excess free volume should increase as the temperature is lowered. This prediction has now been confirmed by high-pressure solubility measurements with CH_4 , C_2H_6 , Ar, and CO_2 in PnBMA, poly(*n*-propyl methacrylate)(PnPMA)($T_g = 35^\circ\text{C}$), and poly(ethyl methacrylate)(PEMA)($T_g = 65^\circ\text{C}$). DMS behavior was observed with CH_4 and Ar in PnBMA at -25°C , and with CH_4 and CO_2 in PnPMA and PEMA at 0°C . C_2H_6 plasticized the polymers, as did CO_2 at higher pressures. Direct evidence for the existence of Langmuir domains is being sought from measurements of quantum isotope effects in permeation.

372. *Particle Deposition in Granular Media* C. Tien **\$145,000** Department of Chemical Engineering and Materials Science **(18 mo.)**

This project is concerned with formulating a theoretical framework for deposition of aerosols from suspensions flowing through granular media and applying the formulation of analyzing problems of practical importance. The specific topics of investigation include: (1) the effect of deposition, particularly the changes in media structure because of deposition, and its effect on granular filtration, (2) the formulation of correlations on collection efficiency, including the effect of particle bounce-off, and (3) the dynamic behavior of aerosol filtration in moving granular media. Included in the last study is the examination of solid flow and solid velocity flow in the presence of transverse pressure gradient.

University of Tennessee Knoxville, Tennessee 37996

373. *Dual Mechanism Bifunctional Polymers: Design, Synthesis, and Application of a New Category of Metal Ion Complexing Agents* S.D. Alexandratos **\$75,000** Department of Chemistry

A new series of ionic polymers has been synthesized with unique applications to separations science, in general, and metal ion separations, in particular. The unifying concept underlying these polymers is that specificity in molecular or ionic separa-

tions is most readily brought about by multifunctional substrates which can participate in multipoint interactions. The dual mechanism bifunctional polymers (DMBPs) form a new category of synthetic multifunctional substrates with enhanced molecular/ionic recognition. These polymers are synthesized with two groups on a given support network, each of which operates by a different mechanism. One mechanism is relatively aspecific, and its primary purpose is to allow the solution species access to the highly specific recognition mechanism. The principal application has been selective metal ion separations from aqueous solutions. The Class I DMBPs are the ion exchange/redox resins; the reduction of certain metal ions to the free metal form is responsible for the resin's specificity. The Class II DMBPs are the ion exchange/coordination resins; different coordinating ligands lead to different metal ion specificities. The Class III DMBPs are the ion exchange/precipitation resins; quaternary amine ligands support different anions electrostatically and lead to the recovery of different metal ions through the precipitation of the metal salts. Polymer-supported synergistic extraction has been observed with the Class III resins.

374. Study of the Surface Properties of Ceramic Materials by Chromatography
G. Guiochon **\$109,988**
Department of Chemistry

The production of advanced ceramic materials for energy research (high structural strength materials above 1400°C) or for sophisticated electronic devices is plagued by the lack of methods permitting the timely elimination of lots that will result in the production of faulty parts. Gas chromatography will be used to determine rapidly and accurately the energy distribution function of the surface of the ceramic powders for a series of probe molecules prior to their use in the manufacturing process. The energy distribution function is related to the chemical composition of the external layer of the solid material and controls the wettability of the particles by and their adhesion to any organic material, such as binder, dispersant, or solvent. Recent results in the theory of large concentration chromatography permit the rapid determination of the thermodynamic and kinetic parameters of the adsorption of probe compounds on an adsorbent contained in a chromatographic column. The energy distribution function is determined directly from the adsorption isotherm. It can be used to calculate other data, such as the monolayer formation energy. Combining the energies determined for a set of probe solutes permits a classification of the surface with respect to similar ones. This could permit us to sort satisfactory materials from unsatisfactory ones. Experimentally, porous layer open tubular columns would be prepared from ceramic powder sample and measurements would be conducted on them using dry or wet carrier gas.

375. Capillary Liquid Chromatography Using Laser-Based and Mass Spectrometric Detection
M.J. Sepaniak **\$66,000**
Department of Chemistry

The focus of this research is on capillary liquid chromatography as a practical separation technique for the analyses of volume-limited, complex samples and difficult to resolve mixtures. The emphasis has been on the development, characterization, and utilization of micellar electrokinetic capillary chromatography (MECC). With this technique, solutes are separated based on their differential distribution between an electro-osmotically

pumped mobile phase and an electrophoretically retarded micellar phase. We have achieved efficiencies in excess of 500,000 theoretical plates/meter with the technique. We have studied factors that influence efficiency and factors that affect selectivity (e.g., micelle-type and mixed mobile phases). Elution range has been extended through the addition of certain organic modifiers to the mobile phase, and procedures have been developed to perform gradient elution. Detection in MECC is complicated by the diminutive volumes of eluted bands (typically about 100 nL). Laser-based fluorescence detection is used extensively in our laboratory. However, we have also utilized fiber optics and a unique laser-etched, on-column flow cell in the development of absorbance detectors. These include a synchronous-type detector and one based on fluorescence inner filter effects (mobile phase is doped with fluorophor in the latter). We have also begun to explore the interfacing of MECC with mass spectrometry.

University of Texas
Austin, Texas 78712

376. Synthesis and Analysis of Novel Polymers with Potential for Providing Both High Permselectivity and Permeability in Gas Separation Applications
W. Koros, D. Paul **\$77,998**
Department of Chemical Engineering

The project focus is synthesis and characterization of a series of polymeric materials for advanced gas separation applications. In addition, the ability to form high-quality integrally skinned asymmetric membranes from these materials is being studied. The fundamental sorption and diffusion factors governing the permeability and permselectivity of the polymers are being measured at pressures up to 1,000 psia with both pure and mixed gas feeds. Materials with extremely high permeabilities for important commercial gases such as hydrogen, carbon dioxide, and oxygen have been identified by systematic variation in the structures of polycarbonates, polyimides, and polysulfones. For some of these materials, attractive permselectivities for gas pairs such as hydrogen/methane, carbon dioxide/methane, and oxygen/nitrogen have been found. 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. If this principle can be demonstrated to be general, it will serve as a basis for establishing a framework to guide the search for advanced materials for future generations of membranes.

Texas A and M University
College Station, Texas 77843

377. Development of Laser-Ion Beam Photodissociation Methods
D.H. Russell **\$83,000**
Department of Chemistry

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. These studies are designed to evaluate the effects of the method of ion production and rates of dissociation of the photoexcited ion on the photofragment ion yield. In addition, the potential analytical utility of laser-ion beam photodissociation for the structural characterization of large biomolecules is being evaluated. These latter studies are being performed on ions formed by fast-atom bombardment (FAB) ionization and include molecules such as chlorophyll a, vitamin B₁₂, small peptides, and glycopeptides (1,500 to 4,000). These studies are performed on modified analytical instruments (e.g., Kratos MS-50TA and MS-902) and a Fourier transform mass spectrometer (Nicolet FTMS-1000).

Texas Tech University Lubbock, Texas 79409

378. *Metal Ion Complexation by Ionizable Crown Ethers*
R.A. Bartsch \$107,500
Department of Chemistry and Biochemistry

Goals of this research are the synthesis of new metal ion complexing agents and their application in the solvent extraction and bulk liquid membrane transport of metal ions. New crown ether carboxylic acids and phosphonic acid monoethyl esters 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 and polymer-supported liquid membrane transport of alkali metal and alkaline earth cations. In addition, the ability of thiacycrown ethers that do not possess ionizable groups to extract trace levels of toxic heavy metal cations is being explored.

379. *Novel Approaches to Ionic Chromatography*
P.K. Dasgupta \$90,000
Department of Chemistry and (13 mo.)
Biochemistry

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. Recent achievements include: (1) the synthesis of a new series of fluorogenic ligands that are also surfactants, permitting a new kind of miscellensitized fluorescence detection of trace metals by post column reaction; (2) the synthesis of new thia-aza ligands that form intensely colored water-soluble complexes with soft acid type metals (these complexes are ideally monitored at wavelengths emitted by solid-state electroluminescent emitters); (3) the development of DC conductivity detection, which uses a stopped-flow technique that does not require stopping the chromatographic run and enables the eluting ions in suppressed ion chromatography to be identified by their electroconductograms (a unique fingerprint generated by a combination of their electrochemical redox behavior and ionic mobility); and (4) the fabrication of the first completely electrochemically suppressed membrane suppressor. Ongoing research concentrates on electroconductographic identification of ions that do not rely on any retention characteristics, a 100% eluent/regenerant recycled suppressed ion chromatography system made possible by the electrochemical membrane suppressor, and novel optical detection schemes.

University of Utah Salt Lake City, Utah 84112

380. *Pulsed Laser Photothermal Spectroscopy of Liquids and Solids*
E.M. Eyring \$78,000
Department of Chemistry

Pulsed laser photothermal spectroscopies have several intrinsic advantages over microphonic photoacoustic spectroscopy (PAS), such as the capacity for the time resolving faster chemical events and easier avoidance of background noise in the desired photothermal signals. A comparison has been made of existing theory with experiment in pulsed laser photothermal spectroscopy of liquids. The dependence of the PA pressure on thermal and elastic properties of the liquid, on laser-beam-transducer geometry, on the speed of sound, and on temperature has been investigated experimentally. Both optical beam deflection detection and a fast, polymeric foil, piezoelectric detector have been used in conjunction with a frequency doubled and tripled Nd:YAG pump laser to follow the radiationless decay of a number of solutes on nanosecond and longer time scales. The optical beam deflection of a helium-neon probe laser beam proved to have advantages over the piezoelectric detection method. When beam deflection is combined with the thermal lens method, the accessible time window for a single experiment can be extended to hundreds of microseconds. This technique facilitates the determination of deexcitation pathways and their quantum yields in liquids and transparent solids. It is being used to investigate the photophysical behavior of dyes that are beginning to be used in laser surgery. The same pulsed laser system will be used to explore the potential of pulsed photothermal radiometry (PPTR) for time resolving relaxation processes in solids.

381. *Hydrophobic Character of Nonsulfide Mineral Surfaces as Influenced by Double Bond Reactions of Adsorbed Unsaturated Collector Species*
J.D. Miller \$72,500
Department of Metallurgy and Metallurgical Engineering

From initial research efforts it was established by transmission FTIR spectroscopy that oleate monomers chemisorbed at a fluorite surface undergo an oxidation/polymerization reaction at elevated temperatures and/or oxygen potentials. These results, while valid, were limited in that the samples were dried, diluted with KBr, and pressed into discs or pellets prior to analysis. Diffuse reflectance FTIR spectroscopic measurements (DRIFT) conducted on an uncompacted dry powder sustained the initial findings from transmission spectroscopy. *In situ* FTIR internal reflection studies are in progress. Characteristic stretching frequencies of adsorbed oleate monomers have been observed *in situ*, and future research will include the examination of the cross-linking polymerization reaction in real time. Thermochemical and electrochemical measurements have been made to further characterize this surface cross-linking polymerization reaction of adsorbed unsaturated collector monomers. If such a reaction can be understood and controlled, the implications are far-reaching. Catalysts or new collectors can be developed to improve the performance, selectivity, and energy economy in nonsulfide mineral flotation systems. Some recent results suggest that such reactions can be catalyzed at the surface of collophanite and other nonsulfide mineral surfaces.

University of Virginia
Charlottesville, Virginia 22901

- 382. *Glow Discharge as an Atomization and Ionization Source***
W.W. Harrison **\$95,000**
Department of Chemistry

This research centers on fundamental and applied studies of the glow discharge as an analytical source for trace element analysis of solid samples. While some work involves the glow discharge as an atom reservoir for atomic absorption and atomic emission, primary focus is on glow discharge mass spectrometry (GDMS). Current projects under way include the design of new ion sources, the reduction or elimination of polyatomic interferences, the analysis of geological materials, and basic glow discharge sputter-atomization studies. Interferences formed in glow discharge plasmas are systematically evaluated by use of a low-pressure collision cell, wherein the polyatomic species are dissociated by energetic collisions with argon atoms. In this way, interferences are greatly reduced and information is obtained on species origin. Alternative discharge gases are being studied for their effect on sputter and ionization rates and for their possible advantages in special applications (such as surface analysis). Getter experiments continue, coupled with the study of geological samples, wherein active scavenger agents are sputtered into the plasma to follow their reactions with traces of oxygen and water vapor. Significant reductions in metal oxide interferences have been observed. An excimer laser is being used for ablation of cathodic samples into a glow discharge plasma, with comparisons to direct glow discharge ablation. The use of lasers for nonconducting samples is of interest.

Virginia Commonwealth University
Richmond, Virginia 23284

- 383. *Compensation for Peak Shifts and Variable Background Responses in Fluorescence Spectroscopy***
S.C. Rutan **\$75,000**
Department of Chemistry

The fluorescence responses observed for polyaromatic hydrocarbon compounds are particularly susceptible to changes in the chemical and physical surroundings of the molecules. Perturbations to the spectral response caused by 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 investigations is the development of mathematical methods that permit the identification and quantification of fluorescent species, despite errors caused by variable background signals and solvent-dependent response shifts. Initial studies have focused on the characterization of existing data analysis methods for background correction and peak shift compensation, based on factor analysis and Kalman filter algorithms. Current efforts are focused on the design and construction of a fluorescence detector based on an intensified diode array for liquid chromatography. This instrument will permit the collection of fluorescence emission spectra as a function of retention time. Data obtained using this instrument will complement earlier studies using thin-layer chromatography.

University of Wyoming
Laramie, Wyoming 82071

- 384. *Solid-Surface Luminescence Analysis***
R.J. Hurtubise **\$85,000**
Department of Chemistry

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. Luminescence, reflectance, and infrared spectroscopy are used to study the interactions. In one set of experiments, the room-temperature phosphorescence of adsorbed compounds is quenched with varying amounts of water in a humidity chamber, and the phosphorescence lifetime and intensity values are measured. Experimental information reveals if static or dynamic quenching is occurring or if a combination of both quenching phenomena are present. In other experiments, the temperature is varied from room-temperature to -180°C in 40° increments, and a variety of luminescence data are obtained. From the data acquired, various luminescence parameters are calculated such as triplet formation efficiencies and the rate constants for phosphorescence. Other work involves the use of cyclodextrins as materials for inducing solid-surface room-temperature phosphorescence, and the measurement of the fluorescence of model compounds on chromatographic columns to study both solution-phase and solid-phase interactions.

Heavy Element Chemistry

Florida State University
Tallahassee, Florida 32306

- 385. *Research in Actinide Chemistry***
G.R. Choppin **\$107,000**
Department of Chemistry

Emphasis is on studying the redox of actinyl(VI) ions by hydroxy organic compounds. The rate laws for the reduction by tropolone, kojic acid, and o-, m-, and p-hydroxy-benzoic acids are being determined. An isotope effect shown as the rate constant in D_2O is three times greater than in H_2O . In addition, a light effect has been seen on the rate constant, which can be attributed to the change in the pK_a of the phenolic group under irradiation. In collaboration with the Argonne National Laboratory Chemistry Division, the reduction of UO_2^{2+} bound to synthetic polyelectrolytes by pulsed radiolysis is under investigation. For all of these systems, the rate equations and models for the reduction mechanisms are being developed. The kinetics of actinide ion dissociation from synthetic and natural polyelectrolytes (humic acids) has been found to have a multiterm rate equation with the percentage dissociation by the various paths depending upon the contact time of the metal ions with polyelectrolyte before dissociation. For plutonium in aqueous solution between pH 4 and 8, an ionic strength range of 0.1 to 4.0 M Pu(V) is found to be the dominant state. The luminescent lifetimes of Eu(III) and UO_2^{2+} are being measured by time-resolved laser spectroscopy to obtain information on the coordination number and the number of residual waters in solution phase complexes of a variety of inorganic and organic ligands.

Comparison of thermodynamic complexation data for Eu(III) with that of Cm-248(III) (by calorimetry) suggests a greater degree of covalency in the curium systems. Calorimetry has been used also to study the synergistic reaction of actinide-TTA complexes with crown ether adducts in benzene solution. These studies provide insight into the role of the water solubility, dielectric constant, and so forth, of the solvent on the synergistic reactions.

University of New Mexico
Albuquerque, New Mexico 87131

386. *Development of Surface Immobilized Ligands for Actinide Separations*
R.T. Paine **\$84,121**
Department of Chemistry

The primary goals of this project are (1) to produce new families of organic extractants for applications in lanthanide and actinide separations, and (2) to prepare solid supported ligands with selective metal ion separation properties. In particular, synthetic pathways are sought to prepare organic solvent soluble extractants with functional groups in 1,2 positions on a carbon backbone. Functional groups of particular interest include phosphoryl, carbonyl, N-oxide, sulfoxide, and sulfone, and difunctional and polyfunctional ligand structures are prepared. The coordination chemistry of model extraction complexes is systematically studied, and the liquid-liquid extraction properties of selected ligands are examined. Results provide interactive information for the design of further improved extractants. Particularly attractive extraction fragment functional groups are then incorporated into inorganic and organic polymers, and the chromatographic separations properties of these solid materials are characterized by spectrophotometric and radiochemical techniques.

Ohio State University
Columbus, Ohio 43210

387. *Molecular Orbital Studies of the Bonding in Heavy-Element Organometallics*
B.E. Bursten **\$49,674**
Department of Chemistry

Significant progress in developing a consistent, simple, and useful scheme for understanding the electronic structure of organoactinide complexes has been made. A calculational approach, the quasi-relativistic $X\alpha$ -SW molecular orbital method, has continued to be a valuable electronic structural probe. In addition, this method has been augmented with other formalisms (DV- $X\alpha$ and *ab initio* methodologies) in the past year. Studies have focused on the dichotomy of roles played by the actinide 5f and 6d orbitals. The latter are principally responsible for the binding of ligands, whereas the former are used to contain metal-based valence electrons. This was tested on a number of novel systems, including $(\eta^5\text{-C}_5\text{H}_5)_3\text{U-CO}$ which is a model of the first discrete actinide carbonyl complex to be synthesized. Before investigating the bonding in transplutonium organometallics (many of which contain three pentahapto cyclopentadienyl ligands), it has been proposed that $(\eta^5\text{-C}_5\text{H}_5)_3\text{An}$ complexes without a fourth ligand will often have a different metal electron configuration than the ligated complexes. Continuing efforts in the chemistry of compounds

containing direct actinide-actinide bonds are proceeding, and collaborations in experimental and theoretical studies with investigators at Los Alamos National Laboratory are under way.

SRI International
Menlo Park, California 94025

388. *Chemistry of Gaseous Lower-Valent Actinide Halides*
D.L. Hildenbrand, K.H. Lau **\$115,974**
Physical Sciences Division **(15 mo.)**

The project objective is to provide accurate thermochemical information for key actinide halide, oxyhalide, and related systems, starting with uranium 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 thorium bromides, the neptunium fluorides and oxyfluorides, and the oxyfluorides of fission product ruthenium. Bonding energy patterns in the uranium fluorides are substantially different from those of the chlorides, bromides, and thorium halides, but the reasons are not yet clear. The entropy data indicate that the gaseous uranium tetrahalides most likely have distorted tetrahedral structures, while the thorium analogs are regular tetrahedra. Additionally, the electronic partition functions of the thorium and uranium monohalides appear to be close to those of the actinide atoms. These patterns will be useful in modeling the thermochemistry of the heavier actinide halides, which will be much more difficult to study.

University of Tennessee
Knoxville, Tennessee 37996-1200

389. *Magnetic Measurements of the Transuranium Elements*
S.E. Nave **\$102,000**
Department of Physics and Astronomy

This project involves a study of the magnetic properties of transuranium metals, alloys, and compounds. Currently research is focused on determining the validity of a crystal-field modified, free ion model to explain the susceptibility of the actinide trihalide and sesquioxide compounds. A computer code has been developed for calculation of the susceptibility based on a crystal field model, using intermediate coupling wave functions and including j-mixing effects. Magnetic actinides have been diluted with nonmagnetic americium to determine the effect of separation of the magnetic species on the low temperature magnetic ordering. Experiments are also in progress on the heavy fermion class of compounds, to study the change from a heavy fermion state to a local moment state with increasing atomic number. A technique has been developed to grow single crystals of actinide halides with milligram masses without loss of material. Research continues on other lossless crystal growth techniques applicable to compounds, metals, and alloys of the heavy actinides, to allow magnetic measurements as a function of orienta-

tion and to provide samples large enough to allow neutron diffraction studies. Work is also in progress to develop new microinstruments for determining the electronic properties of the heavy actinides that are obtained in submilligram sizes because of their scarcity and high specific radioactivity. One such instrument under development is a device to measure susceptibility as a function of pressure.

390. Physical-Chemical Studies of the Transuranium Elements
J.R. Peterson **\$142,000**
Department of Chemistry

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) electrochemical and spectroscopic characterization of unusual oxidation states of lanthanides and actinides in room-temperature, nonaqueous liquid mixtures; (3) x-ray diffraction of actinide materials under pressure; (4) absorption and Raman spectrophotometry of lanthanide and actinide materials under pressure; (5) measurement of the enthalpies of solution of actinide compounds; (6) development of extraction procedures for the recovery of tri- and tetravalent actinides from concentrated aqueous carbonate media; (7) direct or indirect (via radioactive decay) synthesis of actinide compounds containing unusual oxidation states; (8) broader applications of studies to determine the consequences of radioactive decay in the bulk-phase solid state; (9) study of the relationship of natural ion implantation to artificial ion implantation; and (10) growing single crystals of actinide elements and compounds on the milligram scale.

Chemical Engineering Sciences

American University
Washington, District of Columbia 20016

391. Theory of Condensable Gases
J.A. White **\$100,000**
Department of Physics

The project objective is to refine a new theory that calculates the thermodynamic gas, liquid, and supercritical properties and phase diagrams of condensable gases. The theory takes into account the shortness of the range of attractive intermolecular forces in real gases and the enhanced fluctuations at all wavelengths that result. The fluctuations contribute 10 to 30% of the total pressure at many temperatures and densities. This large contribution from fluctuations is currently estimated only crudely and unreliably using empirical formulas to amend mean

field theories or to interpolate between laboratory values found in measurements. The new theory has been found in tests against measurements performed for several gases to make predictions with order of magnitude improvement in accuracy compared with predictions made using existing mean field theories. The theory also makes correct predictions at the critical point as well as elsewhere on the gas-liquid phase diagram. We will further test the theory and use it to produce tabulations of thermodynamic properties of condensable gases for use where measurements are unavailable or insufficiently accurate.

Brigham Young University
Provo, Utah 84602

392. Thermodynamic Study of CO₂-Organic Compound Interaction at High Pressures and Temperatures
R.M. Izatt **\$70,000**
Department of Chemistry

The effects of adding a third component to a binary mixture where one or both components is in its supercritical region are not well understood. In this region, large changes in transport and thermodynamic properties occur with small pressure and/or temperature changes. In an attempt to identify and better understand the effects of adding a third component to binary mixtures, heats of mixing (H^E) are being determined of selected organic compounds with supercritical CO₂ and Freons to which a third component has been added. Two types of experiments are being performed: (1) small (5 mole-percent) amounts of methanol, octanol, octane, a tert-amine, or water are added to the CO₂ or Freon stream prior to mixing with the organic component; and (2) significant (25, 50, and 75 mole-percent) amounts of a third component (toluene) are added to the hydrocarbon stream prior to mixing with the CO₂ or Freon stream. Accurate predictions of ternary H^E values were made using corresponding binary H^E data. The large changes in H^E values in the critical region have been modeled successfully using appropriate equations of state. Molecular dynamic models are being developed for use with these systems. These models are intended to elucidate the fundamental interactions occurring in these systems in the supercritical region.

University of California
Santa Barbara, California 93106

393. Reaction Enhancement of Heterogeneously Catalyzed Reactions by Concentration Forcing
R.G. Rinker **\$167,000**
Department of Chemical and Nuclear Engineering **(30 mo.)**

Experimental and theoretical studies are under way to examine the behavior of nonlinear reacting systems, both isothermal and nonisothermal, under conditions of forced concentration oscillations at constant total pressure. Compared to optimal steady-state operation, concentration forcing can provide higher time-averaged production rates, increased catalyst life, improved selectivity, and lower energy requirements. This study focuses on the synthesis reactions of ammonia, methanol, and methane, and has provided new insight into how surface concentrations of reactants on catalysts can be manipulated under conditions of practical interest, to kinetically accelerate the overall rate of

conversion. For isothermal ammonia synthesis at industrial pressures and temperatures, pure-component feed cycling diminishes production because of catalyst deactivation, while mixture cycling enhances ammonia production by as much as 10% because of increased catalyst activity resulting from active site reconstruction. For nonisothermal ammonia synthesis, such as in autothermal processes, increases in production rate by as much as 150% compared to optimal steady state are obtained, even for pure-component feed cycling. The ammonia synthesis studies have recently been completed, and concentration forcing studies of methanol and methane synthesis are currently being pursued. In the case of methanol synthesis, fixed-bed reactors with well-mixed and nonmixed gas phases are being used. The methane synthesis studies are limited to a fixed-bed reactor with a well-mixed gas phase.

University of California/San Diego
La Jolla, California 92093

394. Premixed Turbulent Combustion

P.A. Libby

\$54,390

Department of Applied Mechanics and Engineering Sciences

This project involves two areas of active research. The first is a continuation of studies of premixed laminar flames. A study of cylindrical premixed laminar flames (i.e., flames with reactants approaching the flame radially, being transformed into products in a thin reaction zone and exiting along an axis of rotation) has been completed. A new flame configuration, counterflowing reactant streams with swirl (either counter- or corotating), is presently under way. Experiments show that swirl has a profound effect on such flames, and our effort is directed at a complementary theoretical analysis. The second area of research concerns a long-term study of premixed turbulent flames in either counterflowing configurations involving one or two reactant streams or in a reactant stream flowing against a solid surface. These flows (1) represent the turbulent analog of the laminar flames which have proven so valuable in fundamental combustion studies; (2) are expected to yield corresponding insight into the properties of turbulent flames; and (3) are rich in variety and interesting phenomena. The first results from this research, an analysis employing a simple description of turbulent transport, have been obtained. Presently two related topics are being pursued. One concerns an extension of the first study, involving a more realistic model of the turbulence. We have encountered severe numerical problems because of the nature of the resultant equations. These problems must be overcome before further progress can be made. A second topic involves application of asymptotic methods to the description of a turbulent stagnation point flow (i.e., the turbulent flow against a solid surface). This work is of interest by itself but is relevant to the case of turbulent flames involving a solid surface.

Clarkson University
Potsdam, New York 13676

395. Analysis and Computer Tools for Separation Processes Involving Nonideal Mixtures

A. Lucia

\$37,000

Division of Research

Analysis can play an important role in the development of reliable computer tools for the simulation and design of separation processes. Previous analysis established uniqueness for single-stage flash processes involving homogeneous mixtures for a variety of specifications. New results have been developed using an algebraic approach that categorizes solutions to multicomponent homogeneous distillations as unique or nonunique according to various column specification sets. Consequences of this analysis, pertinent to the development of reliable computer tools, are currently under investigation. Some convergence results for existing computer tools have been established. Mathematical analysis has been used to explain the multiplicity of vapor-liquid solutions to heterogeneous flash problems and the path connectedness of these solutions. Vapor-liquid-liquid solutions have proven to be unique using pair-wise vapor-liquid equilibrium and geometric methods. Based on this analysis, a new global method for solving three-phase flash problems that is reliable and efficient has been developed. Numerical experiments for three-phase distillations show very complex solution geometry. An understanding of factors that cause difficulties for current computer tools used for the simulation and design of three-phase distillations has been developed. Related mathematical analysis for binary heterogeneous distillations has been completed and is currently under investigation in the multicomponent heterogeneous case.

Colorado State University
Fort Collins, Colorado 80523

396. Study of Improved Methods for Predicting Chemical Equilibria

T.G. Lenz, J.D. Vaughan

\$83,000

Department of Chemical Engineering

A project objective is to be able to accurately determine the equilibrium position of reactions involving large, complex molecules in the liquid state. The equilibrium composition of a chemically reactive system can be determined experimentally, but considering the large number of possible reactions and the associated experimental costs, relying solely on measurement is impractical. Predictive techniques are being studied based on force-field models for gas phase computation, coupled with appropriate standard physical property data, to enable computing liquid reaction thermodynamics. Force-field based techniques have been employed and modified in studying the equilibrium geometries of a variety of acyclic and cyclic dienes (cyclopentene, 1,3-butadiene, 1,3-pentadiene, 1,3-cyclopentadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene) and the methylene-bridged cyclic compounds, norbornane, norbornene, and norbornadiene. These studies were then extended to the Diels-Alder condensation of 1,3-cyclopentadiene. Results indicate that utilizing the force-field model (with modified cyclopentene parameters) provides a satisfyingly accurate alternative to the reported laboratory results for thermodynamic properties ΔH^0 , ΔS^0 , ΔG^0 , and K_a , for the dimerization of 1,3-

cyclopentadiene liquid. These studies are now being extended to yet more complex molecules involving heteroatoms.

Cornell University
Ithaca, New York 14853-5201

397. *Theory and Simulation of Fluids of Associating Chain Molecules*
K.E. Gubbins **\$225,000**
School of Chemical Engineering (18 mo.)

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 will be 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.

398. *Experimental and Theoretical Studies of Dense Fluid Mixtures*
W.B. Street **\$83,000**
School of Chemical Engineering

The primary goals of this research are: (1) to carry out comprehensive thermophysical property measurements on a few strategic pure fluids and mixtures and (2) to develop improved methods for correlating, extrapolating, and predicting dense fluid properties using statistical mechanics and intermolecular potential theory. Recently completed experimental research includes (1) measurements of the PVT properties of CHF₃ and neopentane at pressures to 1,000 bars and (2) speed-of-sound measurements on CFC₃, neopentane, and n-pentane at pressures to 2,000 bars. These measurements were performed in a direct-weighing PVT apparatus which is designed to work from room temperature to 600°C and from 0 to 2,000 bar, and a pulse echo overlap speed-of-sound apparatus which is designed for work from -150 to 250°C and from 0 to 4,000 bar. Measurements are in progress on sulfur hexafluoride. Theoretical work has included (1) applying various equations of state to the PVT data on CHF₃ to test the applicability of different kinds of equations of state to fluid data covering a wide range of conditions and (2) using a multiproperty fitting method to find thermodynamic functions which simultaneously describe PVT, speed-of-sound, and heat capacity data.

University of Delaware
Newark, Delaware 19716

399. *The Generalized van der Waals Theory of Pure Fluids and Mixtures*
S.I. Sandler **\$60,751**
Department of Chemical Engineering

A form of the generalized van der Waals theory and a Monte Carlo computer simulation (on a CRAY supercomputer) have been used to test the fundamental basis of current thermodynamic models, as well as to develop new models. Efforts have so far provided a greater insight into the temperature and density dependence of various terms in an equation of state and

produced new equations of state, including the simplified perturbed hard chain equation. New local composition models, based on computer simulation, have also been developed and are now used to test the resultant activity coefficient models and equation-of-state mixing rules using phase equilibrium data. Work currently in progress, both theoretical and using computer simulation, extends to nonspherical chain molecules, and to mixtures of molecules of greatly different size and functionality. Also, research on the effect of molecular polydispersity on phase equilibrium has resulted in new, efficient descriptions of mixtures as varied as reservoir fluids and aqueous polymer solutions used in biological separations, as well as discovery of a new polymer fractionation phenomenon.

University of Florida
Gainesville, Florida 32611

400. *Theoretical and Experimental Investigations of Fluctuation Thermodynamic Properties of Liquid Solutions*
J.P. O'Connell **\$85,000**
Department of Chemical Engineering (19 mo.)

Fluctuation solution theory is being applied to strongly nonideal liquid mixtures, including aqueous solutions. This theoretical treatment for thermodynamic properties of liquids is rigorous for correlating densities and component activities for such systems. The results have been applied to energy-related solutions such as coal recycle oils with dissolved gases (including hydrogen and carbon monoxide) and aqueous electrolytes similar to those in energy storage devices, industrial waste processing, geothermal power, and mining. Recent results include (1) a new theoretical analysis for the electrostatic effects on all salt solution properties, (2) an accurate model for densities and activities of fully ionized 1-1 salts in water up to high concentrations, (3) a generalized correlation for liquid volumes over wide ranges of temperature and pressure, (4) simple expressions of the partial molar volumes at infinite dilution of aqueous salts to high pressures and temperatures, (5) binary ultracentrifuge equilibrium sedimentation data for nonidealities at low concentrations, and (6) a documented, accurate data base of statistical mechanical correlation function integrals for a variety of systems that will serve as benchmarks for comparisons with all types of solution theories.

University of Illinois
Chicago, Illinois 60680

401. *Development of the Analytic Variational Inequality Minimization (VIM) Equation of State*
G.A. Mansoori **\$72,000**
Department of Chemical Engineering

The primary objective and scope of this research project is to use modern approaches of statistical mechanics to develop new phase equilibrium computational schemes and analytic equations of state for polar, quantum, and associated molecular fluids and fluid mixtures of practical interest. Topics studied include: (1) introduction of an analytic thermodynamic model for fluids with an intermolecular potential consisting of a hard core and an attractive Yukawa tail; (2) development of an

analytic technique for calculation of the hard core molecular diameter of fluids, using experimental entropy data; (3) application of the conformal solution theory of polar fluids for the development of mixing rules applicable for equations of state; (4) development of computational schemes for phase equilibrium calculation of mixtures consisting of species with large molecular size and shape differences and highly polar and hydrogen bonding mixtures; (5) application of the statistical mechanical theory of monomer/polymer solutions for the development of a continuous mixture model for asphaltene and wax deposition from petroleum crude caused by the addition of a completely miscible solvent into the crude; and (6) investigation of the asphaltene deposition and its role in enhanced oil recovery miscible gas flooding processes.

402. Evaluation of Mixing Rules for Viscosity and Thermal Conductivity Using Nonequilibrium Molecular Dynamics

S. Murad **\$88,000**
Department of Chemical Engineering **(18 mo.)**

A computer program to estimate the viscosity of mixtures using the nonequilibrium molecular dynamics (NEMD) technique has been developed based on the time-varying oblique boundary conditions method. In this first stage of the project, simple Lennard-Jones (spherical) mixtures are being studied. Several mixing rules for viscosity are being evaluated by comparing them to the exact NEMD results. The mixtures range from binary mixtures to continuous (many component) mixtures. Continuous mixtures are especially important in the petroleum and biochemical industries. Future plans involve extension of this work to mixtures of spherical and linear compounds, and linear molecules, and finally to mixtures of polar compounds. Computer programs are being developed to allow evaluation of mixing rules commonly used for thermal conductivity. For thermal conductivity, the noncanonical linear response theory is being used. Several different types of mixtures (such as spherical, linear, and polar) will also be studied. They will range from binary to continuous mixtures.

Johns Hopkins University
Baltimore, Maryland 21218

403. Prediction of Thermodynamic Properties of Coal Derivatives

M.D. Donohue **\$123,000**
Department of Chemical Engineering **(18 mo.)**

An understanding of a variety of physical phenomena is necessary in order to predict the thermodynamic properties of chemicals found in coal processing. To this end, the Associated Perturbed Anisotropic Chain theory (APACT) has been developed which incorporates intermolecular forces such as Lennard-Jones, anisotropic interactions caused by dipoles and quadrupoles, and Lewis acid-base or other chemical association forces. The theory was tested by calculating the thermodynamic properties of many systems containing wide ranges of organic molecules. Treatment of various forces in APACT is being rigorously tested by appropriate computer simulations. To date, computer simulation results for nonpolar long-chain molecules verify the treatment of van der Waals forces in APACT. APACT is being reformulated into a group-group interaction

theory, and so far the theory has been successfully reformulated for nonpolar and dipolar molecules. A number of group parameters have been determined. Since the mathematical form of APACT is complex and thus computationally intensive, another theory is being developed which rivals cubic equations of state in simplicity. In addition to theoretical work, experiments are in progress to study the effect of impurities and cosolvents on selective extraction of valuable coal chemicals using high-pressure carbon dioxide and ethane.

Louisiana State University
Baton Rouge, Louisiana 70803-7303

404. Molecular Dynamics Studies of Aromatic Hydrocarbon Liquids

E. McLaughlin, S. Gupta **\$70,811**
Department of Chemical Engineering

This research is concerned with molecular dynamics simulation of fluids containing aromatic hydrocarbons in order to develop and rigorously test predictive models for chemicals encountered in the processing of heavy crudes, tar sands, and/or coal liquids. Focus is on simulation of pure liquids and mixtures containing benzene, toluene, and naphthalene. Progress to date includes systematic simulations of pure dense fluids, using different molecular shapes and intermolecular force models to test two thermodynamic property predictive methods: (1) extension of an existing nonspherical reference based thermodynamic perturbation theory and (2) a new sphericalized potential method. In addition, systematic molecular dynamics simulations have been performed to model liquid benzene successfully with different intermolecular potential models. Computer algorithms developed for these simulations utilize the vector and parallel processing capabilities of general purpose supercomputers efficiently.

University of Maryland
College Park, Maryland 20742

405. Thermophysical Properties of Supercritical Fluids and Fluid Mixtures

J.V. Sengers **\$135,000**
Institute for Physical Science and Technology **(19 mo.)**

This research project is concerned with the development of scientifically based representative equations for the thermophysical properties of fluids and fluid mixtures, including the cross-over of the singular behavior of these properties near the vapor-liquid critical point to the regular behavior of these properties far away from the critical point. Research to develop such equations for the thermodynamic and transport properties of one-component fluids is in an advantage stage. The equations are based on the renormalization-group theory and mode-coupling theory of critical phenomena. An attempt will be made to extend this approach to fluid mixtures.

Massachusetts Institute of Technology Cambridge, Massachusetts 02139

406. *Thermodynamics and Kinetics of Complex Organic Systems*

R.A. Alberty \$128,000
Department of Chemistry (18 mo.)

The objectives of the project are to make thermodynamic calculations on complex organic systems in new ways and to compute the approach to equilibrium using simple rate equations. The new methods involve the use of isomer groups, homologous series groups, new thermodynamic potentials obtained by Legendre transforms, and matrix methods for writing thermodynamic and kinetic equations and making computations. Equilibrium calculations on the polymerization of alkenes on a zeolite catalyst have been followed by use of numerical integrations of rate equations, which incorporate thermodynamics and permit use of various assumptions about either forward or backward rate constants. By adjusting temperature, pressure, starting material, selectivity, and time, various distributions in the gasoline, diesel fuel, and higher carbon number ranges can be obtained. When certain species have specified chemical potentials at equilibrium, it is convenient to use new thermodynamic potentials defined by using Legendre transforms. This reduces the number of components in an equilibrium calculation. Since a whole homologous series can be used as a single component under these conditions, complex systems are easier to understand. For example, the production of polycyclic aromatic hydrocarbons in flames is being investigated by use of equilibrium calculations on subsystems containing an infinite number of species.

National Bureau of Standards Boulder, Colorado 80303

407. *Integrated Theoretical and Experimental Study of the Thermophysical Properties of Fluid Mixtures*

W.M. Haynes \$253,000
Thermophysics Division

The major objective of this research is the development of theoretically based predictive models for complex fluid mixtures. A newly developed field-space conformal solution theory was applied to hydrocarbon mixtures, using cubic equations as the reference pure fluids. In an effort to model systems exhibiting large size differences, the hard sphere corrected corresponding states theory was extended from Lennard-Jones fluids to real fluids. In the area of liquid structure theory, a definitive study of the expansion of the pair correlation function of a fluid under shear was carried out and computer simulation results for the viscoelastic behavior of polyatomic molecules (butanes) were obtained. A phase equilibria model for the extended critical region was applied to ternary and azeotropic mixtures and to interfacial tension calculations; the framework for extending this model to systems exhibiting liquid-liquid equilibria was developed. Theoretically based equations for describing the thermal conductivity critical enhancement for pure fluids in the asymptotically critical and crossover regions were formulated. This mode-coupling theory will be extended to mixtures using only a single parameter to describe the enhancement. A heat of mixing program to study hydrogen bonding in five-membered

ring compounds was initiated. Measurements on binary mixtures of cyclopentane + carbon tetrachloride and tetrahydrofuran with either carbon tetrachloride or chloroform comprise the initial efforts. A preliminary statistical thermodynamic model was developed that describes the qualitative behavior of the partitioning of aqueous two-phase systems.

National Institute for Petroleum and Energy Research (NIPER) Bartlesville, Oklahoma 74003

408. *Thermodynamic Properties by Noncalorimetric Methods*

M.M. Strube \$285,000
Processing and Thermodynamics Division (15 mo.)

The goal of the project is the noncalorimetric determination of thermodynamic properties. This research includes the development or extension of correlational methodologies and the derivation of thermodynamic data from molecular spectroscopy via statistical mechanics. The focus is on methods applicable to polynuclear aromatic compounds, especially those with heteroatoms. The experimental results obtained in recent years at NIPER for the ARTD (Advanced Research for Technology Development) and AER (Advanced Exploratory Research) programs of the Department of Energy, as well as suitable results published by other research groups, are used in the extension of existing group-contribution methods for the reliable prediction of thermodynamic properties. Many processing reactions are performed at high temperatures. The measurement of thermodynamic properties of pure organic compounds at high temperatures (>600 K) by conventional calorimetry is limited by both compound stability and present equipment technology. Thermodynamic property data derived by statistical mechanics do not have these limitations, provided the molecular structure is known and the vibrational frequencies are correctly assigned by proper interpretation of the molecular spectra. Efforts are continuing in extending the capabilities of the molecular spectroscopy laboratory for the collection, interpretation, and assignment of infrared and Raman spectra of polynuclear aromatic hydrocarbons.

State University of New York/Stony Brook Stony Brook, New York 11794

409. *Theoretical Studies of Multicomponent Mixtures: Phase Equilibrium and Transport*

J.M. Kincaid \$78,000
Department of Mechanical Engineering

The purpose of this research is to develop methods for characterizing the thermodynamic and transport properties of multicomponent fluids. The fluids may consist of a finite number, a countable infinity, or a continuum of chemical species. Recent progress includes: (1) a new geometric representation of the dew/bubble conditions of polydisperse fluids that leads to simple algorithms for solving those conditions; and (2) an extension of the Modified Enskog Theory to the case of multicomponent fluid mixtures.

410. Thermophysical Properties of Fluids and Fluid Mixtures

G.R. Stell **\$105,000**
Department of Chemistry

A theoretical investigation of the transport properties of ligands and liquid mixtures continues. The latest results include a study of the shear viscosity of a system of hard-spheres with a poly-disperse size distribution, obtained on the basis of the revised Enskog theory (which is relevant to dense and rare systems). Studies have been completed on (1) transport properties on the Boltzmann equation level; (2) a binary fluid of hard-core square-well particles; and (3) a Lorentz gas of particles with a hard-core square-well interaction between the scatterers and diffusing particles. The investigation of the transport coefficients of Lennard-Jones fluids has yielded predictions in good agreement with computer-simulation results for a variety of thermodynamic states. A quantitative study has been completed of clustering in a fluid of hard-core particles with Yukawa attraction at equilibrium, with results relevant to condensation, gelation, and nucleation. Ongoing work includes an integral-equation approach to the structure and thermodynamics of liquids in pores and next to membranes, as well as free-energy transfer and partitioning of ionic species between two fluid phases.

University of Pennsylvania
Philadelphia, Pennsylvania 19104

411. Thermodynamics of Systems of Very Many Components

E.D. Glandt **\$109,792**
Department of Chemical Engineering **(14 mo.)**

This is a theoretical and computational project concerned with the equilibrium properties of polydisperse liquid mixtures, such as petroleum fluids and polymer solutions and melts. A new, highly efficient Monte Carlo simulation algorithm is proposed that permits a fast and accurate calculation of phase diagrams for mixtures of several or very many components. It has already been applied to binary phase and chemical equilibria, and is now being extended to continuous mixtures. A perturbation theory for narrow cuts was developed in earlier work. The current focus is on the opposite limit, very wide distributions. A predictive theory is being developed in which the properties of a mixture are obtained as a perturbation expansion around the case of an infinitely polydisperse system. Unlike other perturbation approaches, many terms of this expansion can be computed.

Princeton University
Princeton, New Jersey 08544

412. Anisotropy, Charge Distribution, and the Properties of Dense CO₂: Molecular Dynamics Studies

P.G. Debenedetti **\$65,000**
Department of Chemical Engineering **(18 mo.)**

Technical uses of carbon dioxide range from enhanced oil recovery to supercritical extraction. This project is aimed at studying the transport properties of carbon dioxide in the liquid and supercritical regions via computer simulations, in order to understand the relationship between viscosity, thermal conduc-

tivity, translational diffusion, and rotational diffusion, and the geometry and electrical charge distribution of linear molecules. N,V,T molecular dynamics simulations are performed to calculate changes in the viscosity, translational, and rotational diffusion coefficients of rigid, three-site, quadrupolar molecules resulting from the systematic perturbation of quadrupole moment and elongation about the values corresponding to carbon dioxide.

Purdue University Research Foundation
West Lafayette, Indiana 47907

413. Gas-Liquid-Liquid Equilibria in Mixtures of Water, Light Gases, and Hydrocarbons

K.-C. Chao **\$82,000**
School of Chemical Engineering **(15 mo.)**

Polar substances are characterized by the electric poles in their molecules. These poles can interact strongly so that the molecules preferentially orient and segregate. On a microscale, the composition is altered from the bulk value. The local composition of polar fluid mixtures has been simulated with the Monte Carlo method. Square-well molecules of diverse energies and sizes are examined and new models are developed. The validity of some old models is examined. The new models are embedded in the Soave, the Patel-Teja, and the Cubic Chain-of-Rotators equations to extend their usefulness to highly polar fluid mixtures. A new equation of state is obtained for square-well molecules based on the model of coordination number that has been derived from the Monte Carlo simulation. The electric poles of polar molecules interact by coulombic forces to generate a pressure that has a different character in its dependence on T and rho from the nonpolar pressure of dispersion forces. The polar pressure function is obtained by decoupling the pressure of water into a polar pressure and a nonpolar pressure and by generalizing the polar pressure of water. Recent results on the fine structure of water provide the basis to accomplish the decoupling because the interaction potential of water in a polar component and a nonpolar component has been determined. The polar pressure is applied to augment the BACK equation of state for the general description of polar fluids. The augmented BACK equation gives a fair account of the thermodynamics of polar fluids and mixtures, including the VLE, LLE, and VLLE of water plus hydrocarbon mixtures. A new visual phase equilibrium cell with sapphire windows is being assembled. The new apparatus will be useful at pressures up to 60 MPa.

Stanford University
Stanford, California 94305

414. Fundamental Studies of Fluid Mechanics and Stability in Porous Media

G.M. Homsy **\$110,000**
Department of Chemical Engineering

This project treats problems in flow and transport phenomena in porous media whose solutions are important in energy recovery processes. A major review article on viscous instabilities has been written and is already widely referenced. Both experiments and large scale simulations of fingering in miscible and immiscible systems have been completed and several papers

are in press. Current work is focused on understanding displacement processes when mobility profiles are nonmonotonic and/or when viscous and gravity forces compete.

University of Virginia
Charlottesville, Virginia 22901

- 415. Theoretical and Experimental Study of Mixed Solvent Electrolyte Systems**
P.T. Cummings **\$110,000**
Chemical Engineering Department

The objective of this research is to understand and develop predictive tools for the thermodynamic properties and phase equilibria of mixed solvent electrolytes. The approach is a fundamental study, incorporating theory, simulation, and approximate models to the practical problem of salting out in mixed solvents. Statistical mechanical modeling as well as development of analytic expressions for the thermodynamic properties are used to model the behavior of the electrolyte systems. Experimental work is included to enlarge the data base on which to found the models.

University of Wisconsin
Madison, Wisconsin 53706

- 416. Interphase Transport and Multistage Separations**
W.E. Stewart **\$135,000**
Department of Chemical Engineering (18 mo.)

This project has two complementary goals: (1) to provide new predictive capabilities for mass transfer processes and (2) to develop efficient new approaches for computer-aided engineering of these processes. Our recently published asymptotic relations for laminar and turbulent mass transfer are currently being extended to two-phase systems and applied to fractionation efficiency data collected from the literature. A study is in progress on variable-property transport calculations based on optimal reference states calculated from perturbation theory. Adaptive error-sampling weighted residual strategies are being investigated for robust reduced-order simulation and design of stagewise separations. A frequency-domain computation of mass transport in fully developed wall turbulence is under way, to test our asymptotic theory against available measurements of mass transfer power spectra.

Yale University
New Haven, Connecticut 06520

- 417. Computational and Experimental Study of Laminar Premixed and Diffusion Flames**
M.D. Smooke, M.B. Long **\$200,000**
Department of Mechanical Engineering (18 mo.)

The objective of this work is to understand the effects of detailed chemistry and mass transport on the structure and extinction of hydrocarbon flames in a counterflow and an axisymmetric geometry. The work will enable the prediction of extinction limits, space heating rates and flame shapes, height, and width as a function of various parameters. The goal is to obtain a more fundamental understanding of the important fluid dynamic and chemical interactions in flames for use in combustion modeling.

Small Business Innovation Research

The following projects were funded during FY 1988 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.

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.

Bend Research, Inc.
Bend, Oregon 97701

- 418. Novel High-Flux Antifouling Membrane Coatings**
S.B. McCray **\$299,555**
Bioprocess Division (24 mo.)

Membrane-based separations are important in a broad range of market areas and offer many advantages over conventional separation technologies, including greater energy efficiency. However, the full potential for membrane-based operations has not yet been realized. One reason is that membrane performance (flux) often declines with time as the result of membrane fouling. This decline dramatically increases the costs of membrane processes and puts severe limits on the number of separations to which membranes can be applied economically. The cost-effectiveness of many membrane processes could be significantly improved by the development of fouling-resistant membranes. This Phase II project continues a successful Phase I project that demonstrated the feasibility of a promising new approach for increasing the fouling resistance of membranes. During Phase II there will be continued (1) development and testing of fouling-resistant membrane coatings that were developed during Phase I and (2) exploration of other surface treatments. The most promising new membranes will be incorporated into fouling-resistant prototype membrane modules, and long-term tests will be conducted using fouling-prone feed streams. Once the utility of these novel membrane coatings has been demonstrated, the improved membranes will be commercialized.

- 419. High-Flux, High-Selectivity Cyclodextrin Membrane**
P. van Eikeren **\$499,037**
Bioprocess Division (24 mo.)

Membrane-based separations are important in a broad range of market areas and offer many advantages over conventional

separation technologies, including greater energy efficiency. However, the full potential for membrane-based operations has not yet been realized. A principal reason is that current membrane materials exhibit poor selectivity for the separation of molecules of similar size or physical properties. This Phase II project is a continuation of a successful Phase I project aimed at developing a novel ultrathin membrane material that exhibits very high selectivity. The material consists of an array of ordered channels. During Phase I it was demonstrated that this membrane material is capable of separating isomeric solutes. During Phase II, the goals will be (1) to develop further techniques for the fabrication of the membrane, (2) to establish the fundamental relationships between the structure and composition of the novel membrane material and its separation properties, and (3) to develop techniques for the large-scale fabrication of membrane sheets and the incorporation of those sheets into modules.

Precision Analytics, Inc.
Palouse, Washington 99161

420. Continuous Ion Mobility Monitoring as a Liquid Stream Process Sensor
C.B. Shumate **\$500,000**
Research and Development **(24 mo.)**
Division

A novel universal chemical detector is under study. The detector, known as the ion mobility detector (IMD), is being adapted for continuous monitoring of liquid process streams. Such process streams are common in almost all industrial processes. A knowledge of the constituents of these often complex process streams is essential for process control, quality control, and process development activities. The research has indicated that the proposed detector is indeed capable of monitoring a wide variety of chemicals with high resolution. The presently established limits of detection are in the picogram to nanogram range for a variety of compounds. Current work is focusing on establishing the operational limits of the IMD and the optimization of its hardware and software systems. A sampling manifold is also being studied that will interface the IMD with the liquid process stream. The sampling manifold will be capable of basic sample pretreatment and automatic injection of microliters of process liquid into the IMD assembly. The optimized IMD process monitor is expected to find widespread use in chemical, pharmaceutical, plastic, petrochemical, waste treatment, and numerous other industries that use liquid chemicals.

Spectral Sciences, Inc.
Burlington, Massachusetts 01803

421. Development of a Molecular Intracavity Diode Absorption Spectrometer (MIDAS)
N.M. Goldstein **\$484,594**
(24 mo.)

Molecular intracavity diode absorption spectroscopy (MIDAS) offers great potential to meet the need for laboratory and indus-

trial chemical species monitors that are sensitive to parts-per-billion concentrations, species-selective, and compact. The MIDAS technique can be used for a wide variety of environmental conditions, including extremes of temperature, pressure, and high background luminosity. Intracavity absorption is accomplished with an external optical cavity that feeds back a portion of the light emitted by the diode, resulting in multiple traversals by the light in the cavity. By placing the sample within the cavity, absorption of light by the sample is enhanced many orders of magnitude compared to a single pass of the laser beam. Diode lasers have the advantages of being small, extremely stable, solid-state devices. When placed in an external cavity, they can be tuned accurately over a large frequency range, allowing identification and quantification of multiple species in a multicomponent sample. In Phase I, enhancement in a sample absorption line using MIDAS was demonstrated without altering the spectral lineshape or line center location. In Phase II the development issues necessary to turn MIDAS into a sensitive and reliable analytical technique will be investigated. This will lead to the production of a laboratory bread-board instrument that will demonstrate the high sensitivity and selectivity that is possible with MIDAS.

Spire Corporation
Bedford, Massachusetts 01730

422. Novel Electrically Conductive Membranes for Enhanced Chemical Separation
I.-H. Loh **\$49,995**
(6.5 mo.)

Recent reports of the investigation of preparing electromembranes for the presentation of an electric potential barrier to control permeation of charged species have indicated failure of the membranes because of the unstable nature of the materials used in their fabrication. The synthesis of stable conducting polymers by ion implantation processes has been successfully demonstrated. The objective is to investigate the feasibility of using the ion implantation technique to prepare electromembranes. This research is also planned to evaluate the separation efficiency of these newly fabricated electromembranes.

Texas Research Institute
Austin, Texas 78733

423. Synthesis of New Polypyrrones and Their Evaluation as Gas Separation Membranes
P.E. Cassidy **\$49,958**
(6.5 mo.)

The project objective is to synthesize a new tetraamine, 2,2-bis-(3,4-diaminophenyl) isopropylidene, and to polymerize it and tetraaminodiphenyl ether with two anhydrides, hexafluoroisopropylidene-2,2-bis(phthalic anhydride) (6FDA) and pyromellitic dianhydride (PMDA). The resulting new polypyrrones will be characterized, cast in films, and evaluated for gas sorption and transport. The objectives are to develop new polymers with large, rigid segments and to test the ability of these segments to amplify the beneficial effects of the hexafluoroisopropylidene group toward separation of gas mixtures.

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 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 col-

laboration 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, D.C. 20545.

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	\$5,925,000
Oak Ridge National Laboratory	High Flux Isotope Reactor	\$15,600,000
	Transuranium Processing Plant	\$7,185,000
	Electromagnetic Isotope Separations (Calutron) Facility	\$1,770,000
Sandia National Laboratories, Livermore	Combustion Research Facility	\$3,510,000
Stanford University	Stanford Synchrotron Radiation Laboratory	\$8,365,000

ATOMIC SPECTROSCOPY FACILITY (KC-03-01-02)

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

The Argonne spectroscopic facility is designed for high-resolution investigations of the spectroscopic and dynamic properties of atomic and molecular systems. A unique combination of large-scale dispersive instruments with state-of-the-art holographic gratings and pulsed, single-mode, tunable light sources are available. Diode-array and standard detectors are directly interfaced to microcomputers for control of experiments and

pulse-to-pulse normalization of signals which result from multiphoton excitation processes. A pulsed molecular beam apparatus equipped with a time-of-flight spectrometer is available to produce low temperature molecular species. Nd-YAG and excimer lasers are available to pump dye oscillators and amplifiers. Their output is used with frequency doublers and sum frequency generators to cover the 200 to 850 nm spectral

region. The four-wave mixing process in metal vapors and rare gases is used to produce coherent radiation between 118 and 200 nm.

COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists.

PERSON TO CONTACT FOR INFORMATION

J. P. Hessler
 Chemistry Division
 Argonne National Laboratory
 9700 South Cass Avenue
 Argonne, IL 60439

Phone:
 Comm. (312) 972-3717
 or FTS 972-3717

TECHNICAL DATA

Resolving power	
30-foot Paschen-Runge spectrograph	$>5 \times 10^5$
5-meter Czerny-Turner spectrograph	$>10^6$
Tunable dye lasers	$>10^6$
Vacuum-ultraviolet coherent source	$>10^6$
Wavelength range, nm	
30-foot Paschen-Runge spectrograph	200 to 900
5-meter Czerny-Turner spectrograph	120 to 500
Tunable dye lasers	200 to 850
Vacuum-ultraviolet coherent source	118 to 200

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 beams 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 nsec to several msec 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
 Physics Division
 Argonne National Laboratory
 9700 South Cass Avenue
 Argonne, IL 60439

Phone:
 (312) 972-4050
 or FTS 972-4050

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 nsec to 10 msec
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 will be guided by policies established with the help of a users advisory committee. The processing facility may be available for occasional processing of special samples.

PERSON TO CONTACT FOR INFORMATION

Dr. Karl S. Vorres	Phone:
Chemistry Division, Bldg. 211	(312) 972-7374
Argonne National Laboratory	or FTS 972-7374
9700 South Cass Avenue	Telex:
Argonne, IL 60439	TWX 910-258-3285
	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 psec to 10 μ sec. In addition, a 5 psec pulse with the same peak current has been developed. In liquids, transient concentrations up to 20 μ M can be generated with the 25-psec 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. 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:
Chemistry Division	Comm. (312) 972-3471
Argonne National Laboratory	or FTS 972-3471
9700 South Cass Avenue	
Argonne, IL 60439	

TECHNICAL DATA

Energy	
Transient mode	21 MeV
Steady-state mode	14 MeV
Average current	200 μ A (maximum)
Pulse repetition rate	Single pulse to 800 pps (800 pps not possible for all pulses)

Current/pulse		
Transient mode	20 A peak	
Steady-state mode	1.5 A peak	
Picosecond pulse	25 nC (charge per pulse)	
	40 nC (5% satellite pulses at 770 psec)	
Picosecond (5 ps)	7 nC	
Pulse width	5 ps	} transient mode
	25 ps	
	4 to 100 ns	
	.15 to 10 μ s	

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 solely 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. With each of the 30 X-ray and 17 VUV beam ports being further split into two to four beam lines it will be possible, when the NSLS becomes fully operational, to have as many as 100 experiments running simultaneously.

A total of six insertion devices were installed on the X-ray and VUV rings during the past year. These devices, known as either wigglers or undulators, are special magnets which produce synchrotron radiation orders of magnitude brighter than is available from the conventional bending magnets. The insertion devices will be used for microscopy, medical research, materials sciences, spectroscopy, and Transverse Optical Klystron (TOK) experiments.

The NSLS is a facility where a wide range of research techniques are being used by biologists, chemists, solid state physicists, metallurgists, and engineers for basic and applied studies. Among the techniques are EXAFS (extended X-ray absorption fine structure), scattering, diffraction, topography, radiography, fluorescence, interferometry, gas phase spectroscopy, crystallography, photoemission, radiometry, lithography, microscopy, circular dichroism, photoabsorption, and infrared vibrational spectroscopy.

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.

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. In addition to the beam lines constructed by the NSLS staff for general usage, a large number of beam lines have been designed and instrumented by Participating Research Teams (PRTs). The PRTs are entitled to up to 75% of their beam line(s) operational time for a three-year term.

Insertion Device Teams (IDTs) have been formed to design, fabricate, commission, and use wiggler and undulator beam lines. The conditions and terms are similar to those of the PRTs.

General users are scientists interested in using existing NSLS facilities for experimental programs. They are scheduled by an independent beam time allocation committee for a percentage of operating time for each beam line. Liaison and utilization support is provided to the General User by the cognizant beam line.

A program is available to support faculty/student research groups performing experiments at the NSLS as General Users, or performing neutron experiments at the BNL High Flux Beam Reactor (HFBR). The program is designed to encourage new users to these

facilities and defray expenses incurred during exploratory visits to BNL, and while conducting initial experiments at the NSLS and HFBR. It is aimed at university users having only limited grant support for their research.

PERSON TO CONTACT FOR INFORMATION

Susan White-DePace Phone:
NSLS, Bldg. 725B (516) 282-7114
Brookhaven National Laboratory or FTS 666-7114
Upton, NY 11973

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
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

NUCLEAR ANALYTICAL TECHNIQUES (KC-03-02-02)

Atomic and Applied Physics Division
Department of Applied Science
Brookhaven National Laboratory
Upton, New York 11973

This program makes available facilities for the development and application of nuclear analytical techniques. A 3.5-MV electrostatic accelerator provides ion beams

of various gaseous species such as ^1H , ^2H , ^3H , ^3He , and ^4He . Notable features include a triton beam, medium resolution microprobe, rabbit system, and

200-kV ion implanter arranged for simultaneous implantation and analysis. Photon beams with energies from 3 to 20 keV are provided at the National Synchrotron Light Source (NSLS). After current beam line changes are finished, use of either white or monochromatic radiation will be possible. The high brightness of the NSLS X-ray source gives unique opportunities for analytical microprobe methods: determinations of elemental composition using fluorescence techniques are possible with spatial resolutions of $\sim 10 \mu\text{m}$ and detection sensitivities of about 100 parts per billion (mass fraction). Applications in the geochemical, biomedical, and materials sciences are actively supported.

COLLABORATIVE USE

These facilities are open for use by qualified scientists. Arrangements can be made for collaboration with Brookhaven scientists or for independent experiments. Proprietary use is possible on a full-cost recovery basis. In some cases a proposal for review by program advisory committees will be necessary.

PERSON TO CONTACT FOR INFORMATION

K. W. Jones	Phone:
Division of Atomic and Applied Physics	Comm. (516) 282-4588
Department of Applied Science	or FTS 666-4588
Building 815	
Brookhaven National Laboratory	
Upton, New York 11973	

TECHNICAL DATA

200-kV ion implanter	
Range of terminal voltages attainable	20 to 200 kV
Range of maximum ion beam currents available	1 to 20 μA
Ion beams available	Many elements
3.5-MV electrostatic accelerator	
Range of terminal voltages attainable	.3 to 3.5 MV
Range of maximum ion beam currents available	10 to 50 μA
Ion beams available	$^1\text{H}, ^2\text{H}, ^3\text{H}, ^3\text{He}, ^4\text{He}$, and heavier gaseous elements
Repetition rate	DC only
MP-TANDEM accel-decel accelerators	
Range of terminal voltages available	1 to 18 MV
Output currents	Up to 1 μA
Ion beams available	Most elements
Ion energy and charge state	Variable with accel-decel capability
Repetition rate	DC or pulsed with variable repetition rate
NSLS X-ray facility	
Photon energy range	White or monochromatic radiation
Photon flux at target	$\sim 10^9$ photons/ $(\mu\text{m}^2\text{-sec})$ (depends on experimental configuration)

JAMES R. MACDONALD LABORATORY (KC-03-01-03)

Department of Physics
 Kansas State University
 Manhattan, KS 66506

Three accelerators are operated primarily for atomic physics research. These accelerators are a 6-MV EN-Tandem accelerator, a 3-MV Van de Graaff, and a 100-kV accelerator. Either foil or gas poststripping between the 90° and the switching magnets is possible for tandem beams. Available experimental facilities include (1) a 4.5-meter flight tube for impact parameter measurements, (2) a curved crystal X-ray spectrometer, (3) spherical sector and cylindrical electron spectrometers, (4) hydrogen atom and metal vapor oven

targets, (5) low-energy high-charge recoil ion sources, (6) a 45-inch-diameter scattering chamber, and (7) Si(Li), proportional counter, avalanche, and channel-plate detectors. The laboratory is available to users who require the unique facilities of the laboratory for atomic collision experiments. A superconducting LINAC booster to the tandem and a stand-alone Cryogenic Electron Beam Ion Source (CRYEBIS) are under construction and will be operational within the next two years.

COLLABORATIVE USE

Users are encouraged to seek a collaborator on the staff or can submit a brief proposal to the Laboratory Director.

PERSON TO CONTACT FOR INFORMATION

Patrick Richard, Director Phone:
James R. Macdonald Laboratory (913) 532-6783
Department of Physics
Kansas State University
Manhattan, KS 66506

TECHNICAL DATA**EN Tandem**

Beams Most elements
Terminal voltages 0.3 to 6 MV
Output currents Up to 10 μ A, depending
on the ion species and
the charge state
Repetition rate DC or 3-nsec pulses at
rates up to 4 MHz
Magnet limitations ME/q² \leq 150

Output currents Up to 100 μ A
Repetition rate DC only
Magnet limitations None

3-MV Van de Graaff

Beams ¹H or ⁴He
Terminal voltages 0.3 to 3 MV

100-kV Accelerator

Beams Most elements
Terminal voltages 20 to 100 kV
Output currents Up to 10 μ A, depending
on the ion species
Magnet limitations None

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-nsec 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 nsec 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 \sim 400 mJ at 308 nm and \sim 50 mJ at various near-UV and visible wavelengths are available. Detectors having response times of \sim 2 nsec 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.

PERSON TO CONTACT FOR INFORMATION

J. Bentley, Assistant Director Phone:
Notre Dame Radiation Laboratory (219) 239-6117
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 nsec
Time resolution (RC) 2 nsec
Pulse current Up to 1 A
Repetition frequency $0.2 sec^{-1}$
Optical absorption measurements
Spectral region 210 to 750 nm
Sensitivity ± 0.00002 absorbance
Conductivity
pH range 3 to 11
Sensitivity ± 5 mhos/cm

COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists or by a proposal to the laboratory director.

ELECTROMAGNETIC ISOTOPE SEPARATIONS (CALUTRON) FACILITY (KC-03-01-04)

Operations Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

The objective of this facility is to separate and provide multigram quantities of highly enriched separated stable and selected radioactive isotopes, including the actinides, to the research community. Important aspects of the program are process improvement, demonstration of cost-effective methods of isotope enrichment, and chemical recovery procedures. All isotopically enriched samples are distributed through a regular sales program or are circulated to the research community on a loan basis from the Research Materials Collection, administered under the direction of DOE. The program is responsible for the production, distribution, quality control, and reprocessing of the material in the Research Materials Collection. Applica-

tions for the loan of samples from this collection for nondestructive research projects germane to DOE programmatic interests are received at any time.

PERSON TO CONTACT FOR INFORMATION

J. G. Tracy	Phone:
Stable Isotope Enrichment	(615) 574-0425
Operations Division	or FTS 624-0425
Oak Ridge National Laboratory	
P.O. Box 2009	
Oak Ridge, TN 37831	

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 7.0 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) a Penning ion trap apparatus; (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:
Bldg. 5500	(615) 574-4789
Oak Ridge National Laboratory	or FTS 624-4789
P.O. Box 2008	
Oak Ridge, TN 37831-6377	

TECHNICAL DATA

Beams	Most elements
Terminal voltages	0.3 to 7.0 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)

Operations 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/($\text{cm}^2 \cdot \text{sec}$) 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 ^{235}U 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 Isotopes Group. 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.

PERSON TO CONTACT FOR INFORMATION

B. L. Corbett	Phone:
Operations Division	(615) 574-7001
Oak Ridge National Laboratory	or FTS 624-7001
P.O. Box 2008	
Oak Ridge, TN 37831	

TRANSURANIUM PROCESSING PLANT (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 Transuranium Processing Plant (TPP), which is the production, storage, and distribution center for the DOE heavy-element research program. Target rods are fabricated at TPP, irradiated in the High Flux Isotope Reactor (HFIR), and processed at TPP for separation, recovery, and purification of the heavy actinides up through ^{257}Fm . Since their construction in the mid-1960s, TPP 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 TPP 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.

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COMBUSTION RESEARCH FACILITY (KC-03-01-04)

Combustion Sciences Directorate
Sandia National Laboratories, Livermore
Livermore, CA 94550

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 flames processes, as well as research in fundamental chemistry in combustion. (These programs are individually described elsewhere in this publication.) The active program of visitors to the facility including senior researchers, graduate students, and postdoctorals 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 nonpremixed 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 frequently for CARS measurements in flames with large luminous backgrounds (e.g., heavily sooting flames or flames laden with coal particles). A third central laser (Dyeblaster) 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, DOE/Fossil supports programs in coal combustion and related diagnostics development, 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 14 independent experiments, special facility laser systems, a dedicated VAX computer, and access to a Cray computer.

USER MODE

Qualified scientists are encouraged to take advantage of the specialized resources available at 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.

In specific instances, proprietary research can be carried out at 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.

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TECHNICAL DATA

Equipment	Key features
Flashlamp-pumped, tunable dye laser	Long pulse, high energy, high average power: 2- μ sec pulse length 5 J/pulse, 10 Hz Tunable 440 to 620 nm 0.03-nm bandwidth

Equipment	Key features	Equipment	Key features
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 nsec/pulse	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
Low-pressure flames	10 torr to 1 atm Mass spectrometer sampling probe LIF detection of radicals	Combustion bomb	Simulated constant-volume engine combustion
Atmospheric flames	Diffusion and premixed flames	Internal combustion research engines	Highly repeatable environment for homogeneous charge and diesel combustion studies
High-pressure flame	Combination of diffusion flame burner with high pressure flow chamber: Pressures up to 20 atm Slot- or cylindrical-geometry burner 2-D axisymmetric laminar diffusion flame	Experimental diagnostics research facilities	Laser fluorescence laboratory
		Visitor laboratory	Rayleigh, Mie, and Raman 2-D imaging

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 4 GeV storage ring, SPEAR, and the 15 GeV storage ring PEP. SPEAR is dedicated to the production of synchrotron radiation half of its operating time. Operation on PEP is parasitic with the high energy physics program. Presently SSRL has 22 experimental stations on 9 beam lines covering the spectrum from 5 to 45,000 eV. Two 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.

USER MODE

SSRL is currently used by approximately 535 scientists from 114 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, 2066 proposals for research have been received. Demand for experimental time is approximately twice that which can be accommodated.

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TECHNICAL DATA

CHARACTERISTICS OF SSRL EXPERIMENTAL STATIONS*

	Horizontal angular acceptance, Mrad	Mirror cutoff, KeV	Monochromator	Energy range, eV	Resolution Δ/E	Approximate spot size, hgt \times width, mm	Dedicated instrumentation
Insertion Devices Stations							
Wiggler Lines-X-ray							
End stations							
IV-2 (8-pole)							
Focused	4.6	10.2	Double crystal	2,800 to 10,200	$\sim 5 \times 10^{-4}$	2.0×6.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0×20.0	
VI-2 (54-pole)							
Focused	2.3	22	Double crystal	2,800 to 21,000	$\sim 5 \times 10^{-4}$	2.0×6.0	
Unfocused	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0×20.0	
VII-2 (8-pole)							Six-circle diffractometer
Focused	4.6	10.2	Double crystal	2,800 to 10,200	$\sim 5 \times 10^{-4}$	2.0×6.0	
Unfocused	1.0		Double Crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0×20.0	
X-2 (31-pole)							
Focused	2.3	22	Double crystal	2,800 to 21,000	$\sim 5 \times 10^{-4}$	2.0×6.0	
Unfocused	1.0		Double Crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0×20.0	
Side stations							
IV-1	1.0		Double crystal	2,800 to 45,000	$\sim 5 \times 10^{-4}$	2.0×20.0	
IV-3	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0×20.0	Two-circle diffractometer
VII-1	1.0		Curved crystal	6,000 to 13,000	$\sim 8 \times 10^{-4}$	0.6×3.0	Rotation camera
VIII-3	1.0		Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0×20.0	
Undulator lines- VUV/soft X-ray							
V-2	1.5		Rowland circle- multiple grating	10 to 1,200	$\geq 7\%$	6.0×8.0	Angle integrated e^- spectrometer
Undulator lines-X-ray							
PEP 1B	Full		Double crystal	12,000 to 42,000	$\sim 10^{-5}$	0.6×6.0	
PEP 5B	Full	15.0	Double crystal	12,000 to 20,000	$\sim 10^{-5}$	0.6×3.0	Six-circle diffractometer
Bending Magnet Stations							
X-ray							
I-4	2.0		Curved crystal	6,700 to 10,800	0.3×10^{-3}	0.25×0.5	Small angle scattering detector
I-5	1.0		Double crystal	2,800 to 30,000	$\sim 10^{-4}$	3×20	Area detector/CAD-4
II-2 (focused)	4.8	8.9	Double crystal	2,800 to 8,900	$\sim 5 \times 10^{-4}$	1×4	
II-3	1.0		Double crystal	2,800 to 30,000	$\sim 5 \times 10^{-4}$	3×20	
II-4	1.0		None	3,200 to 30,000		3.5×18	
VUV/soft X-ray							
I-1	2.0		Grasshopper	32 to 1,000	$\Delta\lambda = 0.1$ to 0.2\AA	1.0×1.0	
I-2	4.0		6m TGM	8 to 180	$\Delta\lambda = 0.06$ to 3\AA	TBD	
III-1	2.0		Grasshopper	25 to 1,200	$\Delta\lambda = 0.05$ to 2\AA	1.0×1.0	
III-2	4.0		Seya-Namioka	5 to 50	$\Delta\lambda = 0.2$ to 6\AA	2×7	
III-3	8 to 10	4.5	UHV double crystal (jumbo)	800 to 4,500	0.35 to $7\text{ eV}\text{\AA}$	2.0×4.0	
III-4	0.6		Multilayer	0 to 3,000	White or $\Delta\lambda/\lambda=0.3\%$	2×8	Vacuum diffractometer/ lithography exposure station
VIII-1	12		6m TGM	8 to 180	$\Delta\lambda = 0.06$ to 3\AA	1mm^2	Angle resolved e^- spectrometer
VIII-2	5		6m SGM	50 to 1,000	$E/\Delta E \leq 22,000$	1mm^2	Angle resolved e^- spectrometer

*SSRL presently has 24 experimental stations, 22 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 1988 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 1988 equipment funds for Chemical Sciences programs were assigned as follows:

Facility	Equipment funds	Facility	Equipment funds
Ames Laboratory	\$ 600,000	Lawrence Berkeley Laboratory	1,051,000
Argonne National Laboratory	4,130,000	Los Alamos National Laboratory	65,000
Brookhaven National Laboratory	1,545,000	Monsanto Research Corporation-Mound	20,000
Idaho National Engineering Laboratory	15,000	Notre Dame Radiation Laboratory	650,000
		Oak Ridge National Laboratory	1,839,000
		Pacific Northwest Laboratories	170,000
		Sandia National Laboratories, Albuquerque	50,000
		Sandia National Laboratories, Livermore	590,000
		Solar Energy Research Institute	185,000
		Stanford Synchrotron Radiation Laboratory	805,000

INSTITUTION INDEX

- Aerospace Corporation, Los Angeles, CA, 187, 342
 Alabama, University of, Tuscaloosa, AL, 141
 American University, Washington, DC, 391
 Ames Laboratory, Ames, IA, 1-3, 36-38, 73-78, 106-110
 Argonne National Laboratory, Argonne, IL, 4-9, 39-41, 61-64, 79-84, 111-112, 130
 Arizona, University of, Tucson, AZ, 142, 188
 Arizona State University, Tempe, AZ, 143-144, 189
 Atlanta University, Atlanta, GA, 238
 Auburn University, Auburn, AL, 343
 Bend Research, Inc., Bend, OR, 418-419
 Boston University, Boston, MA, 145-146
 Bowling Green State University, Bowling Green, OH, 147
 Brigham Young University, Provo, UT, 270, 344, 392
 Brookhaven National Laboratory, Upton, Long Island, NY, 10-16, 42-47, 65, 85-88, 113-114
 Brown University, Providence, RI, 190, 345
 California, University of, Berkeley, CA, 148
 California, University of, Davis, CA, 191
 California, University of, Irvine, CA, 149-150, 192, 271
 California, University of, Los Angeles, CA, 151, 346
 California, University of, Santa Barbara, CA, 152, 272, 393
 California Institute of Technology, Pasadena, CA, 153, 273-274
 California State University-Fullerton, Fullerton, CA, 239
 California/San Diego, University of, La Jolla, CA, 394
 Chicago, University of, Chicago, IL, 193, 275
 Clarkson University, Potsdam, NY, 395
 Clemson University, Clemson, SC, 154
 Colorado, University of, Boulder, CO, 155, 194-195, 240-241, 276-277
 Colorado State University, Fort Collins, CO, 278-280, 396
 Columbia University, New York, NY, 156, 196, 347
 Connecticut, University of, Storrs, CT, 281
 Cornell University, Ithaca, NY, 197-198, 242, 397-398
 Dartmouth College, Hanover, NH, 157
 Delaware, University of, Newark, DE, 282-283, 348, 399
 Duke University, Durham, NC, 349
 Emory University, Atlanta, GA, 199
 Florida, University of, Gainesville, FL, 350, 400
 Florida State University, Tallahassee, FL, 385
 George Washington University, Washington, DC, 351
 Georgia, University of, Athens, GA, 200
 Georgia Institute of Technology, Atlanta, GA, 201, 243-244, 352
 Hampton University, Hampton, VA, 353
 Harvard University, Cambridge, MA, 202, 245, 284
 Houston, University of, Houston, TX, 158, 354
 Howard University, Washington, DC, 203
 Idaho, University of, Moscow, ID, 355
 Idaho National Engineering Laboratory, Idaho Falls, ID, 115
 Illinois, University of, Chicago, IL, 204-205, 285, 401-402
 Illinois, University of, Urbana, IL, 356-357
 Illinois Institute of Technology, Chicago, IL, 206
 Indiana University, Bloomington, IN, 286-290
 Indiana University-Purdue University, Indianapolis, I, 291
 Iowa, University of, Iowa City, IA, 207, 292
 Jackson State University, Jackson, MS, 208, 246
 Johns Hopkins University, Baltimore, MD, 403
 Kansas, University of, Lawrence, KS, 247
 Kansas State University, Manhattan, KS, 248-249, 358
 Kentucky, University of, Lexington, KY, 209, 293
 Lawrence Berkeley Laboratory, Berkeley, CA, 17-21, 48-52, 66-67, 89-95, 131-132, 137-138
 Lawrence Livermore National Laboratory, Livermore, CA, 53
 Lehigh University, Bethlehem, PA, 294-295, 359
 Los Alamos National Laboratory, Los Alamos, NM, 96, 133-135, 139
 Louisiana State University, Baton Rouge, LA, 159, 250, 296, 404
 Louisville, University of, Louisville, KY, 251
 Louisville Research Foundation, University of, Louisville, KY, 297
 Marquette University, Milwaukee, WI, 160
 Maryland, University of, College Park, MD, 360, 405
 Massachusetts, University of, Amherst, MA, 210, 298
 Massachusetts, University of, Boston, MA, 161
 Massachusetts Institute of Technology, Cambridge, MA, 162, 211-212, 299, 406
 Michigan, University of, Ann Arbor, MI, 213
 Minnesota, University of, Minneapolis, MN, 163, 214-215, 300, 361
 Missouri, University of, Columbia, MO, 301
 Missouri, University of, Rolla, MO, 362
 Monsanto Research Corporation-Mound, Miamisburg, O, 116
 National Bureau of Standards, Boulder, CO, 252, 407
 National Bureau of Standards, Gaithersburg, MD, 164, 216-217, 253, 302, 363
 National Institute for Petroleum and Energy Research (NIPER), Bartlesville, OK, 408
 Nebraska, University of, Lincoln, NE, 165-166, 254
 Nevada, University of, Reno, NV, 303
 New Mexico, University of, Albuquerque, NM, 255, 386
 New Orleans, University of, New Orleans, LA, 218
 New York/Buffalo, State University of, Buffalo, NY, 219, 304
 New York/Stony Brook, State University of, Stony Brook, NY, 220, 364, 409-410
 North Carolina, University of, Chapel Hill, NC, 167, 221, 305, 365
 North Carolina at Charlotte, University of, Charlotte, NC, 168
 Northwestern University, Evanston, IL, 169, 306-309
 Notre Dame Radiation Laboratory, Notre Dame, IN, 22-32
 Oak Ridge National Laboratory, Oak Ridge, TN, 54, 68-71, 97-101, 117-125, 136
 Ohio State University, Columbus, OH, 387
 Oklahoma, University of, Norman, OK, 366
 Oklahoma State University, Stillwater, OK, 367
 Oregon Graduate Center, Beaverton, OR, 170
 Pacific Northwest Laboratory, Richland, WA, 102-103, 126-129
 Pennsylvania, University of, Philadelphia, PA, 222-223, 310-312, 411
 Pennsylvania State University, Lehman, PA, 256
 Pennsylvania State University, University Park, PA, 171, 313-316
 Pittsburgh, University of, Pittsburgh, PA, 224, 257, 317-319
 Precision Analytics, Inc., Palouse, WA, 420
 Princeton University, Princeton, NJ, 172-173, 225-227, 412
 Purdue University, West Lafayette, IN, 228, 258, 320, 368
 Purdue University Research Foundation, West Lafayette, IN, 413
 Rensselaer Polytechnic Institute, Troy, NY, 229, 321, 369
 Rice University, Houston, TX, 230-231, 259
 Rochester, University of, Rochester, NY, 174-175, 232, 260, 322
 SRI International, Menlo Park, CA, 235, 324, 388
 San Diego State University, San Diego, CA, 370
 Sandia National Laboratories, Albuquerque, NM, 72, 104
 Sandia National Laboratories, Livermore, CA, 55-60, 140
 Solar Energy Research Institute, Golden, CO, 33-35, 105
 South Carolina, University of, Columbia, SC, 323
 South Florida, University of, Tampa, FL, 176
 Southern California, University of, Los Angeles, CA, 233-234
 Spectral Sciences, Inc., Burlington, MA, 421
 Spire Corporation, Bedford, MA, 422
 St. John Fisher College, Rochester, NY, 261
 Stanford University, Stanford, CA, 177, 236, 325-326, 414
 Syracuse University, Syracuse, NY, 178, 327, 371-372
 Tennessee, University of, Knoxville, TN, 179, 262, 373-375, 389-390
 Texas, University of, Austin, TX, 180-182, 263, 328-329, 376
 Texas A and M University, College Station, TX, 264, 330-332, 377
 Texas Research Institute, Austin, TX, 423
 Texas Tech University, Lubbock, TX, 378-379
 Toledo, University of, Toledo, OH, 265
 Utah, University of, Salt Lake City, UT, 333-334, 380-381

Vanderbilt University, Nashville, TN, 266
Virginia, University of, Charlottesville, VA, 267, 382, 415
Virginia Commonwealth University, Richmond, VA, 383
Washington State University, Pullman, WA, 183
Washington University, St. Louis, MO, 184
Wayne State University, Detroit, MI, 185-186, 335
Western Michigan University, Kalamazoo, MI, 268

William and Mary, The College of, Williamsburg, VA, 269
Wisconsin, University of, Madison, WI, 237, 336-337, 416
Wyoming, University of, Laramie, WY, 384
Yale University, New Haven, CT, 338-341, 417

SELECTED TOPICS OF GENERAL INTEREST

ACTINIDE CHEMISTRY

4, 124, 130, 131, 132, 133, 134, 135, 136, 385, 386, 387, 388, 389, 390

ANALYSIS

Mass Spectroscopy

108, 112, 115, 117, 118, 119, 121, 126, 128, 352, 363, 368, 377, 382

Miscellaneous

109, 119, 348, 365, 367, 420

Optical Spectroscopy

106, 110, 113, 120, 128, 129, 345, 349, 350, 351, 353, 356, 357, 358, 362, 375, 380, 382, 383, 384, 421

ATMOSPHERIC CHEMISTRY

20, 93, 101

ATOMIC PHYSICS

Collisions

69, 70, 71, 242, 244, 249, 253, 264, 268, 269

Fusion

65, 68, 69, 70, 71, 238, 239, 242, 244, 248, 249, 250, 252, 267, 268

Spectroscopy

39, 61, 62, 63, 64, 65, 66, 67, 72, 240, 241, 243, 246, 251, 255, 257, 258, 260, 262, 263, 265, 267

Theory

68, 238, 239, 245, 247, 248, 249, 250, 252, 254, 256, 259, 261, 265, 266

CATALYSIS

Heterogeneous

41, 49, 75, 76, 77, 91, 100, 104, 216, 224, 231, 270, 277, 281, 282, 283, 284, 285, 286, 289, 292, 294, 295, 296, 298, 300, 302, 306, 308, 309, 310, 316, 317, 318, 319, 324, 325, 326, 327, 328, 329, 330, 331, 332, 335, 337, 339, 340, 393

Homogeneous

73, 79, 87, 89, 96, 188, 292

Organometallic Chemistry (Carbon Monoxide Related)

272, 274, 280, 299, 305, 309, 312, 313, 315, 321, 336

Organometallic Chemistry (General)

46, 73, 74, 92, 94, 95, 105, 188, 271, 273, 276, 278, 279, 288, 293, 297, 301, 304, 307, 311, 322, 323, 333, 338

Surface Chemistry

88, 189, 210, 224, 302

CHEMICAL ENERGY-MISCELLANEOUS

80, 86, 90, 93, 99, 101, 278, 287, 311, 334

COMBUSTION

Dynamics

16, 36, 37, 40, 43, 48, 50, 57, 60, 156, 192, 195, 196, 198, 201, 204, 207, 208, 213, 214, 219, 222, 223, 227, 232, 233, 234, 235, 237

Kinetics

40, 42, 50, 55, 57, 58, 187, 191, 203, 204, 205, 206, 211, 217, 218, 225, 226, 229, 230, 233, 235, 236, 300

Spectroscopy and Analysis

47, 50, 56, 59, 60, 192, 197, 198, 202, 203, 209, 212, 220, 223, 228, 230, 235, 236, 237

Theory and Modeling

36, 38, 40, 43, 48, 50, 53, 55, 56, 57, 58, 187, 193, 199, 200, 206, 211, 213, 215, 225, 227, 417

FOSSIL CHEMISTRY

73, 78, 81, 82, 83, 84, 89, 98, 102, 103, 275, 289, 290, 291, 303, 314, 320, 334

HOT ATOM CHEMISTRY

15, 16, 149, 150, 156, 166, 184

PHOTOELECTRON SPECTROSCOPY

25, 37, 39, 45, 52, 54, 188, 194, 220, 221

RADIATION CHEMISTRY

4, 8, 12, 22, 23, 24, 26, 28, 30, 31, 32, 141, 145, 157, 159, 163, 164, 171, 179

SEPARATIONS

Chromatography

107, 110, 114, 127, 352, 353, 360, 361, 370, 373, 374, 375, 379, 383

Extraction

111, 122, 123, 124, 125, 343, 346, 355, 369, 378

Isotopes

116, 342, 347, 364

Membranes

344, 359, 366, 371, 376, 418, 419, 422, 423

Miscellaneous

354, 372, 381, 395, 416

SOLAR PHOTOCHEMICAL ENERGY CONVERSION

Electron Transfer Rates and Mechanisms

1, 4, 9, 12, 14, 30, 33, 43, 143, 146, 148, 159, 164, 169, 176, 177, 181, 185, 186

Initial Charge Separation in Natural Photosynthesis

2, 5, 6, 7, 10, 141, 161, 165

Inorganic and Organometallic Photochemistry

14, 17, 18, 23, 30, 145, 152, 154, 160, 167, 168, 169, 173, 181, 183, 185

Microheterogeneous Systems

4, 17, 27, 29, 33, 97, 142, 144, 146, 147, 158, 164, 165, 170, 175, 177, 178, 179, 181, 182

Molecular Models

9, 10, 33, 143, 154, 162, 176, 181

Organic Photochemistry

13, 18, 19, 30, 32, 141, 144, 146, 175, 176, 180, 182

Photoelectrochemistry

3, 4, 11, 21, 24, 26, 34, 35, 153, 155, 162, 172, 174, 178, 179, 180, 181

SUPERCritical PHENOMENA

51, 123

SURFACE SCIENCE

36, 41, 43, 44, 49, 52, 109, 115, 126, 128, 153, 162, 172, 189, 190, 210, 216, 231, 302, 330, 374, 381

SYNCHROTRON-RELATED PROJECTS

10, 14, 15, 25, 42, 45, 46, 52, 54, 65, 88, 100, 113

THERMODYNAMIC PROPERTIES

39, 51, 85, 86, 99, 135, 138, 139, 203, 221, 341, 391, 392, 395, 396, 397, 398, 399, 400, 401, 402, 403, 404, 405, 406, 407, 408, 409, 410, 411, 412, 413, 415

TURBULENCE

55, 56, 137, 140, 394, 414, 417

INVESTIGATOR INDEX

- Adams, R.D., 323
 Alberty, R.A., 406
 Alexandratos, S.D., 373
 Alnajjar, M.S., 102
 Andrews, M.A., 87
 Angelici, R.J., 73
 Appelhans, A.D., 115
 Appelman, E.H., 80
 Aris, R., 361
 Armstrong, D.W., 362
 Asano, K.G., 118
 Ashurst, W., 140
 Atwood, J.D., 304
 Autrey, S.T., 102
 Baer, T., 221
 Bair, R., 40
 Balasubramanian, K., 189
 Barker, J.R., 213
 Barteau, M.A., 282
 Bartels, D.M., 8
 Bartholomew, C.H., 270
 Bartlett, N., 90
 Bartsch, R.A., 378
 Basaran, O.A., 122
 Bayfield, J.E., 257
 Becker, R.L., 68
 Beitz, J.V., 130
 Bell, A.T., 91
 Benkeser, R.A., 320
 Bentley, J., 22
 Bercaw, J.E., 273
 Bergman, R.G., 92
 Berkowitz, J., 39
 Bernstein, E.M., 268
 Berry, H.G., 61, 63
 Bersohn, R., 196
 Beuhler, R.J., 44
 Bhatnagar, R., 208
 Bielski, B.H.J., 12
 Bloomquist, C.A.A., 82
 Bocarsly, A.B., 172
 Bohn, P.W., 356
 Bott, J., 187
 Bottcher, C., 68
 Botto, R.E., 83
 Boudart, M., 325
 Bowman, C.T., 236
 Bowman, J.M., 199
 Bowman, M.K., 5
 Braun, C.L., 157
 Brenner, A., 335
 Brezinsky, K., 226
 Britt, P.F., 98
 Brown, L.L., 98
 Brown, N.J., 48
 Brown, S.D., 348
 Browner, R.F., 352
 Brunshwig, B.S., 14
 Bryant, H.C., 255
 Buchanan, A.C., 98
 Bullock, R.M., 87
 Burns, J.H., 125
 Bursten, B.E., 387
 Burwell, R.L., Jr., 307
 Byers, C.H., 122-123
 Calvin, M., 17
 Campbell, C.T., 286
 Cannon, B.D., 129
 Carleson, T.E., 355
 Carlson, T.A., 54
 Carmichael, I.C., 22, 30
 Carnall, W.T., 130
 Carr, R.W., 361
 Casey, C.P., 336
 Cassidy, P.E., 423
 Cattolica, R., 55
 Caulton, K.C., 287
 Cavanagh, R.R., 216
 Celotta, R.J., 253
 Chambers, R.R., 98
 Champion, R.L., 269
 Chandler, D., 148
 Chandler, D.W., 58
 Chao, K.-C., 413
 Chen, J.-Y., 56, 140
 Chen, M.J., 79
 Cheng, R.K., 137
 Childs, W.J., 62
 Chipman, D.M., 22
 Chisholm, M.H., 288
 Choppin, G.R., 385
 Christian, S.D., 366
 Christie, W.H., 117
 Christou, G., 289
 Chu, S.-I., 247
 Clouthier, D.J., 209
 Cochran, H.D., 123
 Cohen, N., 187
 Connick, R.E., 93
 Connolly, J.S., 33
 Cool, T.A., 197
 Cotton, T.M., 165
 Crabtree, R.H., 338
 Cram, D.J., 346
 Creutz, C., 14
 Crim, F.F., 237
 Crosby, G.A., 183
 Crosley, D.R., 235
 Cummings, P.T., 415
 Curl, R.F., Jr., 230
 Curtis, C.J., 105
 Curtis, L.J., 265
 Cutler, A.R., 321
 D'Silva, A.P., 106
 Dahl, D.A., 115
 Dai, H.-L., 222
 Dale, J.M., 119
 Dalgarno, A., 245
 Dasgupta, P.K., 379
 Datz, S., 69
 Davis, M., 40
 Debenedetti, P.G., 412
 Delmore, J.E., 115
 Dibble, R., 56
 Diebold, G.J., 345
 DiMauro, L., 45
 Dittner, P.F., 69-70
 Donohue, D.L., 119, 121
 Donohue, M.D., 403
 Doverspike, L.D., 269
 Dryer, F.L., 225
 DuBois, D.L., 105
 DuBois, M.R., 276
 Dumesic, J.A., 337
 Dunford, R.W., 63
 Dunning, T., Jr., 40
 Durant, J.L., 57-58
 Dworkin, A.S., 101
 Dyrkacz, G.R., 82
 Edelstein, N.M., 131
 Egan, J.J., 85
 Ehrenson, S., 43
 Eischens, R.P., 294
 Ekerdt, J.G., 328
 El-Sayed, M.A., 151
 Elliott, C.M., 278
 Elliott, D.S., 258
 Ellison, G.B., 194
 Endicott, J.F., 185
 Eppley, R.E., 116
 Erpenbeck, J.J., 139
 Espenson, J.H., 74
 Evans, W.J., 271
 Eyring, E.M., 380
 Fajer, J., 10
 Farrar, J.M., 232
 Farrow, R.L., 59
 Fassel, V.A., 106
 Fateley, W.G., 358
 Fayer, M.D., 177
 Feagin, J.M., 239
 Feldberg, S., 11
 Fendler, J.H., 178
 Ferraudi, G.J., 23
 Ferrieri, R.A., 16
 Fessenden, R.W., 24
 Field, R.W., 212
 Fischer, C.F., 266
 Fish, R.H., 89
 Fisk, G.A., 57-58
 Flower, W., 55
 Flynn, G.W., 156
 Fontijn, A., 229
 Ford, P.C., 272
 Fox, M.A., 180
 Frank, A.J., 34
 Franz, J.A., 102-103
 Freeman, D.H., 360
 Frei, H., 18
 Freiser, B.S., 368
 Friedman, L., 44
 Friend, C.M., 284
 Fritz, J.S., 107
 Fujita, E., 14
 Gajewski, J.J., 290
 Gallagher, A.C., 240
 Gallagher, T.F., 267
 Gaspar, P.P., 184
 Gates, B.C., 283
 Gentry, W.R., 214
 Geoffroy, G.L., 313
 Gerstein, B.C., 75
 Gibson, D.H., 297
 Gibson, J.K., 136
 Giese, C.F., 214
 Gilbert, K.E., 290
 Gladysz, J.A., 333
 Glandt, E.D., 411
 Glass, G.P., 230
 Glassman, I., 226
 Glish, G.L., 118

- Goeringer, D.E., 117
 Goldsmith, J.E., 60
 Goldstein, N.M., 421
 Gonzalez, R.D., 285
 Goodman, D.W., 104, 330
 Gordon, B.M., 113
 Gordon, R.J., 204
 Gordon, R.L., 126
 Gorte, R.J., 310
 Gottlieb, C., 202
 Gould, H.A., 66
 Graff, M.M., 201
 Grant, D.M., 334
 Green, N.J.B., 28
 Greenbaum, E., 97
 Greene, E.F., 190
 Griffin, G.L., 296
 Grover, J.R., 45
 Grubbs, R.H., 274
 Gubbins, K.E., 397
 Guiochon, G., 374
 Gupta, S., 404
 Gust, J.D., Jr., 143
 Gutman, D., 206
 Hagaman, E.W., 98
 Haire, R.G., 136
 Hale, B.C., 246
 Hall, G., 15
 Hall, W.K., 317
 Haller, G.L., 339
 Halpern, J., 203
 Hanson, R.K., 236
 Harding, L., 40
 Harold, M.P., 298
 Harris, C.B., 49
 Harrison, W.W., 382
 Havener, C.C., 71
 Hayatsu, R., 83
 Hayes, R.G., 25
 Haynes, W.M., 407
 Helman, W.P., 30
 Henrich, V., 340
 Henry, R.J.W., 250
 Hercules, D.M., 318
 Herman, R.G., 295
 Herron, J.T., 217
 Hessler, J., 40
 Hildenbrand, D.L., 388
 Hioe, F.T., 261
 Hobart, D.E., 133
 Hoffman, D.C., 132
 Hoffman, D.K., 36
 Hoffman, M.Z., 145
 Holmes, H.F., 99
 Holroyd, R.A., 12
 Homsy, G.M., 414
 Horwitz, E.P., 111
 Houk, R.S., 108
 Houston, P.L., 198
 Howard, J.B., 211
 Hrbek, J., 88
 Hug, G.L., 30, 32
 Hulett, L.D., 119
 Hunt, J.E., 112
 Huntley, D.R., 100
 Hupp, J.T., 169
 Hurst, J.K., 170
 Hurtubise, R.J., 384
 Ishida, T., 364
 Izatt, R.M., 392
 Jackson, B.E., 210
 Jackson, W.M., 191
 Janda, K.C., 224
 Jellinek, J., 41
 Jepson, B.E., 116
 Johnson, B.M., 65
 Johnson, E., 136
 Johnson, P.M., 220
 Johnston, H.S., 20
 Jolly, W.L., 94
 Jonah, C.D., 8
 Jones, G., 146
 Jones, K.W., 65, 113
 Jones, W.D., 322
 Jordan, R.J., 292
 Kamat, P.V., 26
 Kanter, E.P., 64
 Kee, R.J., 57
 Keller, O.L., 136
 Kelley, J.M., 126
 Kelley, M.H., 253
 Kern, R.D., Jr., 218
 Kerstein, A.R., 140
 Kestner, N.R., 159
 Keto, J.W., 263
 Kevan, L., 158
 Kiefer, J.H., 205
 Kielkopf, J., 251
 Kincaid, J.M., 409
 Kincaid, J.R., 160
 King, D.S., 216
 King, T.S., 76
 Kispert, L.D., 141
 Klatt, L.N., 120
 Kleinschmidt, P.D., 135
 Klemm, R.B., 42
 Klier, K., 295
 Klingler, R.J., 79
 Koel, B.E., 277
 Koetzle, T.F., 46
 Koros, W., 376
 Kostic, N.M., 1
 Kostroun, V.O., 242
 Koszykowski, M.L., 60
 Koval, C.A., 155
 Kozak, J.J., 27
 Krause, M.O., 54
 Kubas, G.J., 96
 Kung, H.H., 306
 Kwick, A., 46
 Kwok, H.-S., 219
 Lamb, J.D., 344
 Lampe, F.W., 171
 Lane, N.F., 259
 Lau, A.M.F., 60
 Lau, K.H., 388
 Laub, R.J., 370
 Laurendeau, N.M., 228
 LaVerne, J.A., 28
 Lee, Y.T., 50
 Lenz, T.G., 396
 Leone, S.R., 195
 Lester, M., 223
 Lester, W.A., 50
 Lewis, N.S., 153
 Libby, P.A., 394
 Lichtenberger, D.L., 188
 Light, J.C., 193
 Lim, E.C., 186
 Lin, C.D., 248
 Lipsky, S., 163
 Liu, K., 40
 Loh, L.-H., 422
 Long, M.B., 417
 Lucht, R.P., 55-56, 59
 Lucia, A., 395
 Lunsford, J.H., 331
 MacDonald, R., 40
 Madden, K.P., 24
 Madey, T.E., 302
 Madix, R.J., 326
 Mallouk, T.E., 181
 Mansoori, G.A., 401
 Marks, T.J., 307
 Marshall, W.L., 99
 May, M.P., 121
 McBay, E.H., 118
 McBeth, R.L., 83
 McCarty, J.G., 324
 McCray, S.B., 418
 McDonald, D.B., 8
 McDowell, W.J., 125
 McGown, L.B., 349
 McLaughlin, E., 404
 McLuckey, S.A., 118
 McMullan, R.K., 46
 Meisel, D., 4
 Melius, C., 58
 Mesmer, R.E., 99
 Meyer, F.W., 71
 Meyer, T.J., 167
 Michael, J., 40
 Michalski, T.J., 6
 Miller, J.A., 57-58
 Miller, J.D., 381
 Miller, J.R., 4
 Miller, R.J., 103
 Miller, R.J.D., 174
 Miller, W.H., 50
 Montaser, A., 351
 Moore, C.B., 50
 Moore, T.A., 143
 Morss, L.R., 130
 Mottola, H.A., 367
 Moyer, B.A., 125
 Mozumder, A., 28
 Msezane, A.Z., 238
 Muckerman, J.T., 43
 Mullins, D.R., 100
 Murad, S., 402
 Murray, R.W., 365
 Nave, S.E., 389
 Neill, P.H., 84
 Neta, P., 164
 Neuman, R.D., 343
 Newton, M.D., 43
 Ng, C.Y., 37
 Norcross, D.W., 252
 Norris, J.R., 5-7
 Norton, J.R., 279
 Nozik, A.J., 35
 O'Connell, J.P., 400
 Okabe, H., 203
 Otvos, J.W., 17
 Overbury, S.H., 100
 Pagni, R.M., 101
 Paine, R.T., 386
 Painter, P.C., 314
 Palmer, D.A., 99
 Palmer, R.E., 59-60
 Parks, E.K., 41
 Patterson, L.K., 29, 31
 Paul, D., 376
 Payne, G.F., 136
 Pegg, D.J., 262
 Perona, J.J., 122
 Petersen, J.D., 154
 Peterson, J.R., 390
 Phaneuf, R.A., 71
 Pimentel, G.C., 19
 Pitzer, K.S., 51
 Porter, M.D., 109
 Potts, K.T., 369
 Prausnitz, J.M., 138
 Preses, J.M., 15

- Prior, M.H., 67
 Pruett, D.J., 124
 Pugmire, R.M., 334
 Rabideau, P.W., 291
 Rabitz, H.A., 227
 Rack, E.P., 166
 Rahn, L.A., 59
 Ramsey, J.M., 120
 Rathke, J.W., 79
 Raymer, M.G., 260
 Regen, S.L., 359
 Reilly, J.J., 86
 Reisler, H., 233
 Richard, P., 249
 Riley, S.J., 41
 Rillema, D.P., 168
 Rinker, R.G., 393
 Robertson, D.M., 126
 Rodgers, M.A.J., 147
 Rohlfing, E.A., 58
 Ross, A.B., 30
 Ross, H.H., 120
 Rosseel, T.M., 119
 Rosynek, M.P., 332
 Rowland, F.S., 149
 Roy, R., 243
 Ruedenberg, K., 38
 Russell, D.H., 377
 Rutan, S.C., 383
 Rutherford, W.M., 116
 Ryan, R.R., 96
 Sachleben, R.A., 125
 Sachtler, W.M.H., 308
 Sanders, B., 140
 Sandler, S.L., 399
 Sattleberger, A.P., 134
 Sauer, M.C., Jr., 8
 Saykally, R.J., 50
 Scamehorn, J.F., 366
 Schaefer, H.F., 200
 Scheeline, A., 357
 Schefer, R., 56
 Schmidt, K.H., 4, 8
 Schmidt, L.D., 300
 Schrader, G.L., 77
 Schrock, R.R., 299
 Schuler, R.H., 28, 31
 Schwarz, H.A., 12
 Schwarz, J.A., 327
 Scott, C.D., 123
 Scott, L.T., 303
 Scott, R.G., 83
 Scott, T.C., 122
 Sears, T., 47
 Seely, G.R., 144
 Selegue, J.P., 293
 Seltzer, S., 13
 Sen, A., 315
 Sengers, J.V., 405
 Sepaniak, M.J., 375
 Sharp, P.R., 301
 Shaw, R.W., 120-121
 Shepard, R., 40
 Sherrow, S.A., 124
 Shirley, D.A., 52
 Shriver, D.F., 309
 Shumate, C.B., 420
 Sieck, L.W., 363
 Silbey, R., 212
 Simmons, G.W., 295
 Simonson, J.M., 99
 Small, G.J., 2
 Smalley, R.E., 231
 Smith, A.V., 72
 Smith, D.H., 121
 Smith, G.P., 101
 Smith, R.D., 127
 Smith, S.J., 241
 Smooke, M.D., 417
 Sneddon, L.G., 311
 Soderholm, L., 130
 Somorjai, G.A., 21
 Spiro, T.G., 173
 Springston, S.R., 114
 Starace, A.F., 254
 Stell, G.R., 410
 Stern, S.A., 371
 Stevens, B., 176
 Stewart, W.E., 416
 Stille, J.K., 280
 Stock, L.M., 275
 Stoffel(s), J.J., 126
 Streett, W.B., 398
 Strube, M.M., 408
 Struve, W.S., 3
 Styris, D.L., 128
 Sudeman, N.K., 103
 Suib, S.L., 281
 Sullivan, J.C., 130
 Sutherland, J.W., 42
 Sutin, N., 14
 Talbot, L., 137
 Tang, J., 5
 Tanis, J.A., 268
 Tardy, D.C., 207
 Templeton, J.L., 305
 Thaddeus, P., 202
 Thomas, E.W., 244
 Thurnauer, M., 5
 Tiede, D.M., 5, 7
 Tien, C., 372
 Tiller, F.M., 354
 Todd, P.J., 117
 Tollin, G., 142
 Toth, L.M., 124
 Trahanovsky, W.S., 78
 Trebino, F.P., 60
 Trifunac, A.D., 8
 Tripathi, G.N.R., 31
 Truhlar, D., 215
 Tully, F.P., 58
 Turner, J.A., 35
 Turro, N.J., 347
 Urasa, I.T., 353
 Vager, Z., 64
 Valentini, J.J., 150, 192
 van Eikeren, P., 419
 van Willigen, H., 161
 Vane, C.R., 69
 Vannice, M.A., 316
 Vaughan, J.D., 396
 Vollhardt, K.P.C., 95
 Vorres, K.S., 81, 84
 Wacker, J.F., 126
 Wagner, A., 40
 Walker, R.L., 121
 Wasielewski, M.R., 5, 9
 Watson, R.L., 264
 Watts, R.J., 152
 Wayland, B.B., 312
 Webber, S.E., 182
 Weir, D., 32
 Westbrook, C.K., 53
 Weston, R.E., 15
 Whitaker, T.J., 129
 White, J.A., 391
 White, J.M., 329
 White, M., 45
 Whitten, D.G., 175
 Whitten, W.B., 120
 Wiberg, K.B., 341
 Wilkes, W.R., 116
 Williams, T.F., 179
 Winans, R.E., 82-84
 Winefordner, J.D., 350
 Winkler, J., 14
 Winter, T.G., 256
 Wishart, J., 12
 Wittig, C., 234
 Wolf, A.P., 16
 Woodward, J., 97
 Wrighton, M.S., 162
 Yates, J.T., Jr., 319
 Yeung, E.S., 110
 Yonker, C.R., 127
 Young, J.P., 120-121
 Young, L., 61
 Zingg, S.P., 101
 Zittel, P.F., 342

