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# Summaries of FY 1986 Research in the Chemical Sciences

September 1986

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

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Division of Chemical Sciences

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

The purpose of this publication is to inform those interested in 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. This publication includes projects supported by both the Chemical Sciences budget and that portion of the Nuclear Sciences budget which is administered by the Division of Chemical Sciences.

These summaries provide to members of the scientific and technical public and interested persons in the legislative and executive branches of the Government a means for becoming acquainted, either generally or in some depth, with the Chemical Sciences program. Areas of research supported by the Division are to be seen in the section headings, the listing of "Selected Topics of General Interest," and the summaries themselves. Energy technologies that can be advanced by use of the basic knowledge generated in this program are provided in the "Selected Topics" list and also (by reference) in the summaries.

Chemists, physicists, chemical engineers, and others who are considering the possibility of proposing research for support by this Division will find the publication useful for gauging the scope of the present program in basic research and the relationship of their interests to the overall program. Proposals that expand this scope will also be considered or directed to more appropriate offices. The research summarized here is intended to add significantly to the knowledge base on which successful energy technologies can grow. For this purpose, scientific excellence is a major criterion applied in the selection of research supported by the Division of Chemical Sciences. Another important consideration is the emphasizing of chemical, physical, and chemical engineering subdisciplines which are advancing in ways that produce new information related to energy, needed energy data, or new ideas.

The program takes place in several different kinds of performing organizations. About half the projects are at DOE laboratories and half at universities and industrial laboratories. In DOE laboratories, most of the researchers are fully engaged in this work, while most university and industrial researchers necessarily divide their time among duties involving this research, other research, teaching responsibilities, etc.

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

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

# Chemical Sciences Division
# Office of Energy Research
# U. S. Department of Energy
# Washington, D.C. 20545

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| **Isotope Preparations** | | |
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*On detail from the National Bureau of Standards.

†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 into the interactions of radiation with matter in all forms but particularly with gases and liquids. The photochemical research is devoted largely to studies with visible radiation aimed at the capture and conversion of solar energy. This encompasses such fields as artificial photosynthesis, photoinduced electron transfer reactions in homogeneous and heterogeneous media, photoelectrochemistry, and photocatalysis. 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 new and 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 research kinetics, as well as the reactions of clusters. Research efforts in molecular structure, spectroscopy, and theoretical chemistry are also well represented in this program.

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 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, ions, and simple molecules. 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.

## 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, and (3) the conversion of biomass and related cellulosic wastes. The disciplines of organic, bio-, inorganic, physical, thermo-, and electrochemistry are central to this program. 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.

### 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.

### Isotope Preparations (KC-01-02)

The Isotope Preparations program is dedicated to the production of research quantities of isotopically enriched research materials by way of the Electromagnetic Isotope Separations (Calutron) facility, the High Flux Isotope Reactor (HFIR), and the Transplutonium Processing Plant (TRU). These facilities are described in the Special Facilities section of this book. These research materials are made available to an international user community from a sales inventory, by loan from a Research Materials Collection, and by cost-free allocation from the DOE Research Materials/Transplutonium Program Committee.

### Heavy Element Chemistry (KC-01-02-03)

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 under pressure. This research is performed principally at the National Laboratories because of facilities required for handling radioactivity.

## Chemical Sciences Division

### Stanford Synchrotron Radiation Laboratory (KC-01-03)

Support for the operation of the Stanford Synchrotron Radiation Laboratory (SSRL) is provided through this category. Access to this facility is possible by the submission of individual proposals directly to SSRL. Evaluation and award occur through a peer review process conducted by SSRL's program committee, a representative group selected by users of the facility. The research carried out by the users represents a broad field of disciplines not confined to those supported by the other categories listed above. As a consequence, most of the research projects using SSRL are funded by other DOE offices, other agencies and private sources.

# LABORATORY ADMINISTRATION

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

## AMES LABORATORY

Iowa State University
Ames, IA 50011

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**Heavy Element Chemistry**

**Stanford Synchrotron Radiation Laboratory Operation**

# SUMMARIES OF FY 1986 RESEARCH IN THE CHEMICAL SCIENCES

## NATIONAL LABORATORIES

## Photochemical and Radiation Sciences

### Ames Laboratory
### Iowa State University
Ames, Iowa 50011

**Fundamental Interactions Program** **$325,000**

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

The project objective is measurement of rates and elucidation of mechanisms of electron-transfer reactions similar to those involved in plant photosynthesis and in other processes for conversion of solar into chemical energy. Selective binding of redox-active transition-metal complexes to metalloproteins results in novel electron-transfer systems, in which the synthetic and native metal sites can undergo intramolecular redox reactions over long distances, in protein environments whose structural and thermodynamic properties are determined by spectroscopic and electrochemical measurements. We are working to discern the following key factors that affect the rates of electron transfer: intersite distance, nature of the intervening medium, temperature, and thermodynamic driving force. A particularly novel aspect of this project is the possibility of comparing ground-state and excited-state electron-transfer reactions under similar conditions. [0.5 FTE]

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

This project focuses on (1) the relationship between structural organization and the intermolecular interactions between pigments that dictate electronic energy and electron transfer processes in artificial and naturally occurring photosynthetic aggregates and (2) the nature of electronic energy transfer (e.g., coherent vs. incoherent) when it occurs over macroscopic distances such as in molecular crystals or long chain chromophoric polymers. A variety of laser spectroscopies are used, such as optical hole burning, fluorescence line narrowing, four-wave mixing and two-photon spectroscopies. Solid-state hole burning and four-wave mixing (CARS, CSRS) are used to understand the intermonomer interaction, electronic and vibrational structure, and photophysics of artificial chlorophyll dimers and of the special pairs of photosynthetic reaction centers. The special pair is the primary electron donor of the reaction center, but the nature of its lowest energy excitonic state is poorly understood. In addition to these photosynthetic problems, nonlinear laser spectroscopies are used in novel ways to engineer unidirectional electronic energy transfer over macroscopic distances. [2.38 FTE]

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

Picosecond fluorescence spectroscopy is used to study excited-state decay processes of dye molecules adsorbed on semiconductors and insulators. Since an accurate theory has not yet been developed for excitation transport and trapping in two dimensions (i.e., on surfaces), we have been obtaining detailed fluorescence profiles for well-characterized dye and excitation trap coverages on surfaces to assess the limitations of the present theory. We have also examined fluorescence decays and picosecond-resolved transient absorption of dyes adsorbed on semiconductors, and have found that dye-to-surface mode nonradiative decay is an extremely efficient process on single-crystal $TiO_2$ and ZnO. Thus, such nonradiative decay is a likely origin of low photocurrent yields in liquid junction cells. To ascertain the physical mechanism of this decay, we have analyzed fluorescence profiles emitted by rhodamine dyes adsorbed on $TiO_2$, ZnO, gold, and aluminium. All of these profiles decay rapidly (i.e., lifetime $\leqslant$ 200 picoseconds), and none are well-described by single-exponential decay laws even in the limit of extremely low dye coverage. On the semiconductors, the profiles correspond to an analytical decay law arising from trapping of dye excitation by a two-dimensional array of semiconductor surface states. The decay mechanism on metals is under investigation. [2.37 FTE]

### Argonne National Laboratory
Argonne, Illinois 60439

**Chemistry Division** **$4,980,000**

#### *4. Preparation of Organisms, Photosynthetic Pigments, and Biological Materials of Unusual Isotopic Composition*
*H.L. Crespi, D. Tiede, J.R. Norris*

The project objective is the production of photosynthetic and other microorganisms substituted with biologically important rare stable isotopes, such as $^2H$, $^{13}C$, $^{15}N$, $^{17}O$ or $^{18}O$, and $^{25}Mg$. Large quantities of green algae, cyanobacteria, and photosynthetic bacteria are routinely available in unnatural isotopic composition involving single or multiple isotope substitutions. These unusual organisms (and the compounds obtained from them) have significant applications in novel magnetic resonance studies, small-angle neutron scattering, and resonance Raman spectroscopy. Typical applications include the study of chlorophyll, photosynthesis, biomimetic photochemistry, and bacterial photosynthesis reaction centers. Of particular relevance is the ability to provide material for the growth of protein single crytstals containing unusual isotopes. Genetically engineered bacteria are also cultured to give good yields of the proteins. [1.0 FTE]

### 5. *Gas-Phase Radiation Chemistry and Photochemistry*

*C.D. Jonah, D.B. Bartels*

This project uses pulse radiolysis to measure rate constants for simple free-radical reactions of importance in atmospheric and combustion chemistry. With this technique it is possible to measure the kinetics at high pressures and over the temperature range of 330 to 1250 K, a range no other single experimental technique can easily span. The reaction rates of OH and OD radicals with CO and $C_2H_4$ have been measured. Reactions of OH radicals with other species are under investigation; other radical species are also investigated. The rate of production of hydrogen atoms from the reaction from OH + CO and the reaction of hydrogen with $O_2$ are also under study. In addition to the practical importance of these reactions to combustion, the data serve as an excellent test for reaction theories because of the rigorous restrictions provided by the wide temperature range and the use of two hydrogen isotopes. [2.9 FTE]

### 6. *Chlorophyll and Photosynthesis Research*

*J.J. Katz, T.J. Michalski, J.R. Norris, J.E. Hunt, M.K. Bowman*

The project objective is to understand chlorophyll function in light-energy collection, energy transfer, and charge separation in the conversion of light energy to chemical energy in photosynthesis. This understanding requires study of the basic physical and chemical properties of the chlorophylls. We are particularly interested in the coordination interactions of the chlorophylls because we believe that the self-assembled chlorophyll species formed by the expression of these forces are responsible for the characteristic features of *in vivo* antenna and reaction center chlorophyll. We are currently studying: (1) the structure of chlorophyll/water micelles by small-angle neutron scattering; (2) the applications of heavy-ion desorption mass spectroscopy ($^{252}Cf$ plasma desorption mass spectroscopy, $^{252}Cf$–PDMS) to chlorophyll and photosynthesis problems; (3) the chemical physics of chlorophyll systems, which included magnetic resonance and infrared spectroscopy studies related to chlorophyll aggregates; and (4) the chemical properties of chlorophyll cations and the synthesis of model systems intended to mimic important features of *in vivo* reaction center and antenna chlorophyll. [3.0 FTE]

### 7. *Electron Transfer and Energy Conversion and Storage*

*J.R. Miller, D. Meisel*

This project has two principal objectives: (1) the fundamental understanding of electron transfer in molecules, especially at fixed distances and (2) elucidation of the chemical mechanisms that control various photochemical energy conversion and storage schemes. Pulse radiolysis is used to measure the effects of distance, energy, and molecular structure electron transfer rates. To fix distances of electron transfer, the reacting groups are imbedded in rigid matrices or are attached to rigid spacer molecules. Mechanisms of enrgy conversion schemes, particularly in organized assemblies and microheterogeneous systems, are studied using fast laser techniques and the Argonne National Laboratory linac facility. Redox processes at the interface between the assembly (polyelectrolyte, micelle, semiconductor colloid, and so forth) and the electrolyte are studied in detail, to understand the factors that control electron transfer through the interface and the ensuing chemical processes that follow charge injection in or out of these microsubphases. [10.3 FTE]

### 8. *Physicochemical Investigation of Photosynthesis*

*J.R. Norris, M.K. Bowman, D. Tiede, J. Tang, T.J. Michalski, M. Wasielewski, H.L. Crespi*

The major concern of this project is the extraction of chemical work from sunlight. The structure of natural photoreaction centers and the primary fast chemistry and physics that occur during photosynthesis are studied in detail. The structure of the reaction center from *Rhodopseudomonas sphaeroides* R-26 is being determined with x-ray diffraction. Time-domain spectroscopy is used to meausure distances, orientations, and dynamics within the molecular components that participate in the transfer of electrons. These studies are guided by structural information available from x-ray diffraction. Electron transfer that occurs on the time scale ranging from a few picoseconds to longer is probed by optical and magnetic techniques. New magnetic methods and theory are developed specifically to characterize ultrafast charge separation in artificial and natural chemical systems. Charge separation in single crystals of the protein reaction centers of several photosynthetic bacteria is investigated by magnetic and optical spectroscopy. [6.5 FTE]

### 9. *Reactive Intermediates in Condensed Phases*

*A.D. Trifunac, C.D. Jonah, M.C. Sauer, Jr., M.C. Thurnauer, D.B. Bartels, D.B. McDonald, K.H. Schmidt*

The project objective is to provide a fundamental understanding of chemical reactivity by studying a broad range of reactive intermediates in the liquid and solid state. The chemistry studied is relevant to understanding (1) the breakdown in dielectric liquids and (2) charge separation, recombination, and charge transfer phenomena, which are the basis of chemical and biological processes of energy storage and utilization. The identity, structure, and dynamics of unstable transients important in radiation chemistry and photochemistry are studied. The chemistry of ground-state and excited-state paramagnetic species is examined. The role of the solvent in the chemical reactivity of highly charged reactive species, like electrons, is studied theoretically and experimentally. The details of radical reactions are examined using electron and nuclear spin dynamics. Redox reactions of actinides and lanthanides are studied using pulse radiolysis. Essential tools used in this project are the Argonne high-current picosecond electron linac, the pulsed Van de Graaff accelerator, and innovative time-resolved magnetic resonance and laser techniques, which are being developed and applied to these problems. [16.6 FTE]

### 10. *Artificial Photosynthesis*

*M. Wasielewski, J.R. Norris, T.J. Michalski, D. Tiede*

The goal of this research is to develop and fully characterize molecular assemblies in the laboratory that will mimic and even improve on natural photosynthetic energy conversion. This work combines several interrelated aspects of artificial solar energy conversion. Molecules designed to serve as models of the natural photosynthetic energy conversion system are synthesized. These chemical reaction centers aid in the structural and mechanistic understanding of the natural process of photosynthesis. The photophysics and photochemistry of our models are investigated by placing emphasis on the light-induced electron-transfer reactions. Advanced spectroscopic techniques, such as picosecond spectroscopy and time-domain magnetic resonance, are essential in the characterization of these ultrafast processes. The primary photosynthetic processes are investigated to integrate the information obtained from the artificial laboratory systems with new knowledge of natural photosynthesis. [3.9 FTE]

## Brookhaven National Laboratory
## Upton, Long Island, New York 11973

### Department of Applied Science $1,110,000

### 11. *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 by chlorophylls in photosynthesis. The extensive body of data acquired to date for chlorophylls is equally applicable and relevant to the chemistry of the broad class of porphyrins and, in particular, to their functions in catalyzing nitrogen assimilation, hydroxylations, and carbon dioxide conversion. The work also seeks to exploit the chemistry of the recently discovered compounds of iron, cobalt, and nickel chlorins, isobacteriochlorins, and corphines that mediate these reactions. The work combines theoretical and experimental techniques to predict, identify, and characterize transients and mechanisms in these catalytic conversions. Experimental methods presently include spectroelectrochemistry, magnetic resonance (ESR, ENDOR, AND NMR), x-ray diffraction, and synchrotron radiation (EXAFS and edge studies), and are closely supported by several theoretical methods (SCF-MO-PPP, IEH, and INDO). [7.0 FTE]

### 12. *Electrochemistry and Photoelectrochemistry*

*S. Feldberg*

The project objective is 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 theoretical implications of extended heterogeneous electron transfer (EHET), where electrons actually jump several angstroms from the electrode into solution, have been investigated and the effects of EHET at an ultramicroelectrode are now being considered. Simulation of cyclic voltammetric behavior of a variety of electrochemical kinetic schemes (with emphasis on cyclic voltammetric behavior) and simulation of the rotating ring disc electrode are examined as part of a long-time interest in simulation of electrochemical phenomena. Development of a new technique for investigating very fast heterogeneous electron transfer, laser-induced-temperature-jump coulostatics, comprises theoretical and experimental investigations. Theoretical and experimental studies consider the electrochemical and transport properties of ferrocenium/ferrocene couples in polyethylene oxide and the feasibility of using this material as the electrolyte in a photoelectrochemical solar conversion system. Spectroelectrochemistry and ellipsometry of polyaniline (an electronically conducting polymer) were used to elucidate the mechanism of electrochemical switching (between the conducting and insulating states) and combined with theoretical efforts to describe some unique electrochemical behavior of this new class of materials. We are continuing analysis of the effects of picosecond irradiation of semiconductor systems. [3.3 FTE]

### 13. *Chemical Properties and Reactions of Mono- and Dinuclear Ferrocene Derivatives*

*R.B. Klemm*

The project objective is preparation of metallocenes and investigation of their properties, particularly as they relate to the oxidation and reduction of water. Preparation of ferrocene derivatives with potentials high enough to oxidize water under neutral or slightly acid conditions are under way. For the reduction of water, mechanisms of the generation of hydrogen from [1.1] ferrocenophanes with strong acids are investigated. Kinetics of hydrogen formation were studied and specific rates for three ferrocenophanes were derived. Results indicate that the orientation of the protons on the iron atoms has a significant effect on the reaction. It is therefore believed that understanding this reaction will enable further modification of the ferrocenophane so that hydrogen might be obtained from weak acids and perhaps even water. Current studies focus on the effect of deuterated acid on the rate of hydrogen evolution and on the composition of the gas to determine the extent of H–D exchange in the ferrocenophane. [2.6 FTE]

### Chemistry Department $2,550,000

### 14. *Radiation Chemistry*

*R.A. Holroyd, H.A. Schwarz, B.H.J. Bielski*

Transient chemical species, such as radicals and ions in unusual oxidation states, are important in many chemical reactions. This project studies the behavior of these transient species, produced by pulse radiolysis or photolysis. Principal areas of investigation are: (1) photoionization and properties of electrons in dielectric fluids; (2) nature of transition metal ion–hydroperoxyl radical complexes; (3) other reactions of the hydroperoxyl radical; and (4) formation and reactions of transition metal complexes in unusual oxidation states. Studies of transition metal complexes and hydroperoxyl radicals are relevant to reactions for conversion of solar to chemical energy and to the understanding of homogeneous catalysis. Studies of electrons in fluids are important in understanding the basic processes of radiation chemistry and in developing new detectors for use in high-energy physics and in EXAFS measurements. [7.0 FTE]

### 15. *Photochemical Energy Conversion and Solution Kinetics*

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

Transition-metal complexes may undergo facile outer-sphere electron-transfer reactions and function as homogeneous catalysts for the formation or activation of small molecules such as $H_2$ and $CO_2$. In addition they have long-lived excited states that can be formed by the absorption of light in the visible region of the spectrum. Such complexes are therefore attractive candidates for use in photochemical energy conversion and storage systems. This project encompasses fundamental studies of the reactions and structures of transition-metal complexes in their ground and excited states. The efficient conversion of light into chemical energy requires that useful reactions of electronically excited molecules be favored over physical deactivation processes and chemical back-reactions. The project objective is the study of the rates and mechanisms of electron-transfer reactions of excited- and ground-state complexes and the physical deactivation processes of excited complexes to elucidate the effects of the structures of the reactants, the thermodynamic changes accompanying the reaction, and the dynamic properties of the medium on the reaction rates. Because the overall efficiency of a photochemical process is also determined by the nature and rates of the chemical reactions subsequent to the initial photochemical electron transfer, mechanistic studies of the thermal reactions of transition-metal complexes, particularly those in high and low oxidation states are conducted, and the individual steps are modeled. [9.5 FTE]

### 16. *Energy Transfer in Chemical Kinetics*

*R.E. Weston, J.M. Preses*

The distribution of energy among translational, rotational, vibrational, and electronic degrees of freedom in reacting species has a profound effect on the rates of chemical reaction they undergo. For this reason, collisional transfer or radiative loss of energy is an important part of many reaction mechanisms. In this project, pulsed laser radiation is used to produce translationally energetic (hot) atoms or highly vibrationally excited molecules. Rates of collisional energy transfer from these energetic species are determined using infrared fluorescence, laser-induced fluorscence, and diode laser absorption spectroscopy. In addition, vacuum-ultraviolet radiation from the Dynamic Spectroscopy Beamline of the National Synchrotron Light Source is used to study electronically excited states of molecules and photoionization of atomic species. Assistance to outside users of this facility is also supported by this project. [5.0 FTE]

### 17. *Research in Hot Atom Chemistry*

*A.P. Wolf, R.A. Ferrieri*

The fundamental and practical importance of understanding the chemistry occurring between energetic (hot) atoms and molecules has prompted recent effort in this project to seek new methods to generate these species. A novel approach that relies on ion beam sputtering has been developed to produce 7 to 8 eV $O(^3P)$ atoms. Studies on the reactions of these atoms with alkyl-substituted alkenes are presently yielding information on the energy dependence of the reaction channels. Isolation and detection of stereoisomer products also provides insight into intermediate stability at high energy. Conventional nuclear methods are also implemented to obtain kinetic and mechanistic information in the following areas: (1) reactions of thermalized $^{13}N(^4S, ^2D, ^2P)$ atoms with simple atmospheric gases; (2) reactions of recoil $^{11}C$-atoms with complex organic molecules; (3) stereochemical consequences of recoil halogen atom substitution reactions; and (4) energy dependence of phenylcarbene rearrangements. Application of nucleogenic atoms and their reactions toward labeling molecules with short-lived positron-emitting radionuclides also yield a novel approach to studying the kinetics of surface-catalyzed reactions. These labeled molecules are used as transient probes for ultrasensitive surface detection, and provide a means to study fundamental surface chemistry at exceedingly low surface coverages. [3.7 FTE]

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| **National Synchrotron Light Source Department** | **$5,150,000** |

### 18. *National Synchrotron Light Source Operations and Development*

*M.L. Knotek*

The project objective is to support operations and development of the National Synchrotron Light Source (NSLS). Operations cover: (1) operation and maintenance of the two NSLS electron storage rings and its associated injector combination of linear accelerator-booster synchrotron; (2) operation and maintenance of the photon beam lines of the vacuum ultraviolet and x-ray storage rings; and (3) the technical support of experimental users. Development of the NSLS includes further improvement of the storage rings by means of new developments in high-resolution photon optics, state-of-the-art monochromators, x-ray mirror systems, detectors, and so forth. The NSLS storage rings will provide extremely bright photon sources, several orders of magnitude more intense in the vacuum ultraviolet and x-ray regions than conventional sources. An extensive research and development program is necessary to optimize performance characteristics and to develop new beam line instrumentation that will permit users to take advantage of the unique research capabilities to be offered by this important facility. This research and development effort also provides information that will support the construction of the beam lines and devices to be funded under the Phase II construction project. [49.7 FTE]

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

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| **Chemical Biodynamics Division** | **$920,000** |

### 19. *Artificial Photosynthesis*

*M. Calvin, J.W. Otvos*

The project objective is to devise a synthetic system for storing the energy of visible light. The system involves a photoinduced electron transfer across a phase boundary, mimicking natural chloroplasts in the process of photosynthesis. Our approaches include the use of various kinds of phase boundary in stabilizing the primary products of photosensitized electron transfer reactions, thus preventing their back reaction. Ultimately, the energy stored in these products will be channeled by appropriate catalysts into the decomposition of water into hydrogen and oxygen, or the reduction of $CO_2$ to functionalized organic products. Phase boundaries under study include: (1) lipid bilayer walls of phospholipid vesicles (used to keep the initial photoproducts separate), (2) surfaces of colloidal silica and various polyelectrolytes, and (3) surfaces of functionalized colloids. The surface potential of polyelectrolytes and polymeric colloids can be used to retard back-reactions of the primary products of electron transfer. They may also have advantages over colloidal silica by virtue of their adjustable charge density and useful pH range. Finally, we are studying the catalysts that will be necessary on both sides of the electron transfer assembly. We focus on porphyrin complexes of manganese, which can exist in several oxidation states and may therefore be useful in catalyzing the conversion of the primary oxidized photoproduct to oxygen. [6.0 FTE]

### 20. *Photon Conversion Through Storage of Metastable Molecules*
*H. Frei*

The goal of this project is to find chemical systems that permit indefinite storage of long-lived electronically excited molecules. Photoinduced chemical storage of electronically excited species has potential for efficient, indefinite storage of solar photon energy, including energy at near-infrared wavelengths. Thermodynamics and quantum efficiency of singlet oxygen–endoperoxide systems are studied using tuned lasers to induce reaction, and FT-infrared absorption and near-infrared chemiluminescence spectroscopy to monitor the chemistry. Direct observation through its near-infrared chemiluminescence of singlet delta $O_2$ expelled from endoperoxides upon excitation with ultraviolet laser pulses in nonpolar and aqueous solutions permits study of the decay of the retrieved electronically excited oxygen molecules in real time. Intracavity cw dye laser near-infrared luminescence excitation spectroscopy is being developed to determine barriers and efficiencies to adiabatic decomposition of singlet oxygen storing molecules through high vibrational overtone excitation on the ground electronic surface. [1.2 FTE]

### 21. *Chemistry of Electronically Excited Molecules*
*G.C. Pimentel*

This research investigates the chemistry and energy movement as it occurs on electronically excited hypersurfaces. Since both natural and artificial photosynthetic processes depend upon the chemistry of electronically excited molecules, these studies aid in the design of systems for chemical storage of photon energy. Cryogenic solids furnish particularly favorable environments for the study of light-initiated and reaction-initiated movement between and on electronic hypersurfaces. Reactants under study include $O_2(^1\Delta_g)$, with furanes, mercury, cadmium, and zinc atoms; with haloalkanes and haloalkenes; and $NH(^1\Delta$ and $X^3\Sigma)$ with dimethylacetylene. The reaction between imidogen and dimethylacetylene provides various isomeric products and an interesting system for hypersurface mapping. Focus is on energy storage using near infrared light, photochromism, and hypersurface mapping. Temporal aspects of electronically excited transient intermediates are examined using nanosecond infrared spectroscopy. [6.0 FTE]

## Materials and Molecular Research Division $440,000

### 22. *Photochemistry of Materials in the Stratosphere*
*H.S. Johnston*

This research is concerned with fundamental gas-phase photochemistry, with application to molecules and radicals that occur in the stratosphere. 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. This research has applications to molecular dynamics, to problems of atmospheric ozone, and to the role of trace gases other than carbon dioxide on the "greenhouse effect". [5.0 FTE]

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

This project explores photocatalyzed chemical reactions that take place at the solid–liquid interface. Focus is on the photodissociation of (1) water to produce hydrogen and oxygen, and (2) nitrogen to form ammonia. The purpose of these studies is to explore the mechanism of photoassisted surface reactions and to establish the optimum conditions (of surface structure, composition, temperature, and reactant mixture) to maximize the rate of production of desired chemicals (hydrogen, oxygen, and ammonia). Materials used include iron oxides, silicates, and oxides of tungsten and molybdenum. [2.3 FTE]

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

**$2,810,000**

### 24. *Quantum Mechanical Studies of Radiation-Produced Intermediates*
*D.M. Chipman, I.C. Carmichael*

Electronic structure calculations based on *ab initio* quantum mechanical principles are used to characterize the fundamental microscopic properties of matter that ultimately govern the processes experimentally observed in areas such as radiation chemistry, photochemistry, chemical kinetics, and various types of spectroscopy. In particular, molecular geometries, potential energy surfaces, reaction mechanisms, intermolecular forces, and other fundamental properties are calculated for various species involved in reacting chemical systems. Emphasis is on the study of unique characteristics of free-radical intermediates occurring in many chemical reactions. Recently, a comprehensive study of the *m*-benzosemiquinone radical anion has shown that the most stable form is actually a low-symmetry structure with properties more like a substituted phenoxyl radical than a normal semiquinone. The behavior of this species is influenced by a low-energy barrier to intramolecular interconversion bewteen two equivalent forms. Vibrational frequencies and spin densities have been calculated for members of the isoelectronic series of $AH_3$ and $AMe_3$ radicals and radical ions with $A = B^-$, C, $N^+$; $Al^-$, Si, and $P^+$. These have provided accurate predictions of stretching frequencies for deuterium modes and deuterium-isolated hydrogen modes and have also revealed erroneous claims of experimental observations for some of these radicals. [2.6 FTE]

### 25. *Organic Photochemical Processes*
*P.K. Das*

This project focuses on kinetic and mechanistic details of organic photoreactions in solution. The time-resolved techniques of laser flash photolysis and pulse radiolysis are used to observe and probe various photointermediates on nanosecond and longer time scales. The transients of interest include singlet, triplet, and doublet excited states; exciplexes; ion pairs; radicals; biradicals; and zwitterions. The roles played by these transients in such photoreactions as cycloaddition, fragmentation, small-molecule extrusion, oxygenation, hydrogen abstraction, and electron transfer are elucidated. Studies in progress include energy transfer involving triplets and doublets, ring opening leading to isomerization and enlargement, energy partitioning in bichromophoric molecules, energy migration and trapping in polymers, and intra-ion-pair proton transfer. Model substrates include cyanoaromatics, carbonyl and thiocarbonyl compounds, three- and five-membered heterocycles, polyenes ending with heteroatoms, and polymers containing carbonyl groups. A specific aim is to sort out the stereoelectronic and thermodynamic factors that affect energy storage, conversion, and dissipation in the excited-state bimolecular interactions. Favorable competitions between ion separation and reverse electron transfer in photogenerated ion pairs are being established as important aspects of a general mechanism for prompt chemical transformations under photosensitization. [5.3 FTE]

### 26. *Inorganic Photochemical Processes*
*G.J. Ferraudi*

The photochemical properties of various coordination complexes are elucidated. This project includes characterization of: (1) the effect of intense magnetic fields on photochemical reactions, (2) the sequential two-photon photochemistry of coordination complexes, and (3) the photophysical and photochemical properties of complexes with macrocyclic ligands. Magnetic field-induced perturbations of orbitally degenerate excited states are used as probes of the electronic restrictions in different types of reactions (i.e., photosubstitution, electron transfer, and energy transfer reactions). Sequential biphotonic excitations are used to study the excited-state photoreactivity. Correlations between the results of time-resolved experiments and quantum yields provide a unique insight into the excited-state photochemical reactivity, which cannot be explored with monophotonic experiments. Photophysical and photochemical studies are conducted with a number of macrocyclic complexes (phthalocyanines, pyrazines, and more simple macrocycles) and complexes bound to polymers. These compounds exhibit direct or sensitized photochemical or sensitized photochemical redox reactivity for excitation in the visible region of the solar spectrum, and are candidates for use in solar energy conservation. [6.0 FTE]

### 27. *Microwave Studies of Radiation-Produced Radicals*
*R.W. Fessenden, Madden K.P.*

Electron spin resonance (ESR) spectroscopy is used to study radical structures, reaction mechanisms, reaction kinetics, and electron spin interactions of radicals produced by *in situ* radiolysis. ESR spectra provide definitive information on geometric and electronic structure and acid–base properties. Time-resolved ESR experiments with pulsed radiation provide information on rates of radical reactions and the strengths of electron spin interactions that lead to bonding. Recent measurements on cyclohexadienyl radicals and the related system $H_2CN$ containing $^{13}C$ show that some aspects of the electronic structure of this type of radical are not yet understood; this problem will be attacked at the theoretical level. Microwave dielectric absorption methods are used to determine the degree of charge separation in photochemical intermediates to explain changes in reaction mechanism with solvent polarity. A number of excited complexes (exciplexes) have been studied and found to have smaller dipole moments than previously believed. Implications of this finding are being investigated. Microwave absorption is also being used to measure the yield, properties, and kinetics of charge carriers photoinjected into semiconductor particles and films. This method provides information not otherwise available on systems of importance to solar energy conversion. [9.5 FTE]

### 28. *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. In small molecules (carbon sulfide) the photochemistry is sensitive to the site of excitation, but in larger molecules (benzene and cyclohexane) the photochemistry is much less sensitive to the mode of excitation. These observations are extended by (1) studying molecules exhibiting several possible distinct sites for excitation (formamide) and (2) examining minor pathways in the photochemistry of larger molecules, such as ejection of $H^+$ from benzene and cyclohexane upon carbon 1s excitation. We are reexamining the production of atomic ions from molecules such as benzene just at the carbon 1s absorption threshold, since our observations disagree with those of others. [0.9 FTE]

### 29. *Photochemical and Photoelectrochemical Processes for Light Energy Conversion*
*P.V. Kamat*

Photocatalytic transformations in homogeneous and heterogeneous systems are investigated to develop and improve the performance of photochemical and photoelectrochemical systems useful in solar energy conversion. Time-resolved photoelectrochemical experiments are performed using nanosecond laser spectroscopy, pulse radiolysis, and spectroelectrochemistry to elucidate the mechanistic features and kinetic details of interfacial processes: photosensitization, phototransformations of adsorbed species, and photocorrosion at singlet crystal and colloidal semiconductor surfaces. Recently a $TiO_2$ microelectrode system containing both a dye electron scavenger and $SCN^-$ hole scavenger, has been shown to enhance the yield of photoelectrochemical oxidation and reduction. Visible light-induced photoelectrochemical polymerization of 1-vinyl pyrene also has been demonstrated at a n-GaAs semiconductor electrode for the first time. Development of modified electrode surfaces with photosensitive materials and characterization of their photophysical, photochemical, and electroanalytical properties will aid in the elucidation of the photosensitization process. With the aid of computer simulations, the dynamics of $H_2$ and $O_2$ evolution in homogeneous and heterogeneous photochemical systems is being elucidated. This is approached by isolating the kinetics of single reaction components and extrapolating to the dynamics of coupled systems. Examples of such systems involve $H_2$–catalyst interactions and the redox chemistry of viologens. [5.9 FTE]

### *30. Statistical Theories of Reacting Systems*
*J.J. Kozak*

A theoretical study of diffusion-controlled reactive processes on compartmentalized systems is conducted to determine and quantify the factors affecting the efficiency of chemical-dynamic processes related to energy storage and transfer in such systems. The approach is based on the theory of finite Markov processes and effects associated with the size of the reaction space; its dimensionality and symmetry are considered explicitly and exactly. The role of potentials, sequestered reaction domains, local imperfections, cage effects, and the number and distribution of reaction channels is studied to clarify experiments in which organizates may be used in photochemical processes to effect the storage of solar energy. In order to apply the theory of finite Markov processes to study processes in real time, it has been necessary to relate the approach to the time-dependent master equation. Calculations carried out for discrete versus continuous time processes have clarified the factors at play in experimental studies of excitation, migration, and trapping on networks of chromophores (e.g., the chlorophyll antenna system). This theoretical framework has also provided a means of calculating first-order rate constants for a series of anion radicals undergoing dehalogenation via intramolecular electron-transfer reactions. [4.9 FTE]

### *31. Track Effects in Radiation Chemistry*
*J.A. LaVerne, A. Mozumder, R.H. Schuler*

The radiolytic production of hydroxyl radicals in the heavy-ion radiolysis of water has been used as a probe of particle track structure. Differential hydroxyl yields for different particles at the same linear energy transfer (LET = -dE/dx) decrease by 10 to 20% for each increase in charge of the irradiating particle. After correcting for $\delta$ rays, the LET dependence of hydroxyl yield pertinent to the trackcore is common to all of the particles studied at low energies. At high LETs hydroxyl yield is considerably greater than that found with fast electrons, suggesting a large concentration of an oxygen species in heavy particle tracks. This could have important biological consequences. A statistical method using experimentally determined oscillator strength distributions has been used to determine that the density-normalized mean range of low-energy electrons ($\sim$100 eV) in water varies as vapor < liquid < solid. All effects of phase on electron range disappear at energies above a few keV. The density-normalized mean ranges of low-energy electrons in the rare gases also increase with increasing mass of the medium. The probability of free-ion formation in liquid argon is two orders of magnitude less when irradiated with high-energy neon and iron ions as compared to fast electrons. [3.3 FTE]

### *32. Influence of Ordered Molecular Assemblies on Photochemical Processes*
*L.K. Patterson*

The effects of molecular organization on photochemical and photophysical processes are investigated in various heterogeneous systems: spread monolayers, liquid crystals, and micelles. Information gathered from these different systems is used to elucidate the types of changes in reactant–host lipid interactions to exercise control over the behavior of excited states and subsequent reactions. Focus is on spread monolayers, because they provide the best means for control of molecular organization and simultaneous monitoring. Steady-state and time-resolved luminescence techniques and polarization spectroscopy are used. Data from application of such techniques are compared to the thermodynamic record of the monolayer as reflected in force-area isotherm measurements. It is then possible to correlate changes in photophysical behavior to alterations in organization of the microenvironment (e.g., lipid packing or phase transition). Energy transfer, electron transfer, and diffusional processes are studied by these methods in porphyrin- and pyrene-bearing systems in various lipid matrices. Photochemical studies are conducted to characterize product formation from photoreactions and to measure quantum yields under various conditions in liquid- and solid-like monolayers. [5.8 FTE]

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

The Radiation Chemistry Data Center (RCDC) provides information services on radiation chemistry and photochemistry, compiles and evaluates data, and publishes data reviews. The scientific literature reporting kinetic, spectroscopic, quantum yield, or radiation yield data for irradiated systems is included. Bibliographic and numeric data bases are assembled and used for on-line searching, to answer inquiries, and to prepare publications such as bibliographies and data tables. The *Biweekly List of Papers on Radiation Chemistry and Photochemistry*, the printed version of the RCDC Bibliographic Data Base (RCDCbib), is distributed to subscribers. Numeric data bases are built for property data on metastable chemical species and a chemical registry file (RCDCreg) is maintained for all compounds, ions, and radicals represented in the data files. Automated procedures are used with RCDCbib, RCDCreg, and the numeric data bases to aid the compilation, evaluation, and publication process. Data for primary processes involving excited states in condensed phases are compiled and evaluated. Rate constants for reactions of transient radicals in aqueous solution are compiled and evaluated in collaboration with scientists from other laboratories. Other projects involving outside collaborators include compilation and evaluation of (1) quenching rates for excited states of metal complexes in solution and (2) one-electron reduction potentials for radicals in aqueous solution. [4.0 FTE]

### *34. Radiation-Induced Chemical Reactions*
*R.H. Schuler, G.N.R. Tripathi, L.K. Patterson*

A wide variety of chemical reactions induced by the absorption of ionizing radiation is examined using the Notre Dame Radiation Laboratory's broad base of highly developed chemical and instrumental methods (absorption spectrophotometric, conductivity, ESR, laser resonance Raman, and chromatographic methods) for examining intermediates in time-resolved studies and for analysis of ultimate products. Emphasis is on the production and reactions of short-lived radical intermediates in the radiolytic oxidation and reduction of organic materials in aqueous solution. Focus is on prototype systems such as the radicals produced from phenols, anilines, and quinones. ESR experiments provide information on the electron distribution in these radicals and Raman experiments on their vibrational structure.

The latter also allow monitoring of the reactions of specific intermediates that do not have distinguishable absorption spectra. These time-resolved studies are complemented by studies of the overall radiation chemistry of typical oxygen- and nitrogen-containing aromatic systems using chromatographic methods. In particular, products of bimolecular processes that dominate the radical chemistry at high radiation dose rates are being examined. [19.3 FTE]

## Solar Energy Research Institute
## Golden, Colorado 80401

### Solar Fuels Research Division $730,000

### *35. Photophysics and Photochemistry of Porphyrins and Model Systems for Artificial Photosynthesis*
*J.S. Connolly*

This project focuses on some fundamental aspects of electron-transfer processes of excited states in donor–acceptor systems. Detailed photophysical and photochemical studies on light-induced electron transfer are conducted in porphyrin-based molecular assemblies (linked and unlinked) as synthetic models of photoreaction centers. Our goal is to gain a better understanding of the molecular properties required for efficient light-induced electron transfer and subsequent charge stabilization. Laser flash photolysis, fluorescence, and spectroscopic studies are performed on covalently linked porphyrin–quinones and on their unlinked constituents to sort out the effects of photophysical properties, redox potentials, molecular geometry (distance and orientation), temperature, and solvent properties on the kinetics and mechanisms of the forward and reverse processes. In addition, we are performing comparative studies on linked and unlinked components incorporated into vesicles and other microheterogeneous assemblies to determine the requirements for vectorial electron transfer in artificial photosynthesis. [1.5 FTE]

### *36. Modified Semiconductor Electrodes for Solar Energy Utilization*
*A.J. Frank*

We are investigating: (1) fundamental problems of the photoinstability of n-type semiconductors; (2) high overpotential associated with the water splitting reaction; (3) low quantum yields resulting from recombination of electron–hole pairs at the electrode–electrolyte interface; and (4) energetics and dynamics of charge transfer through conductive polymer films on electrode surfaces. Interfacial chemistry, energetics, and surface dynamics are established by photoelectrochemical measurements, end-product analyses, and surface characterization studies. Information obtained from the physicochemical investigations provides guidance for strategies to chemically modify the semiconductor surface to improve photostability and kinetics of desirable redox reactions. The approach of coating the semiconductor surface with electrically conductive polymers in combination with catalytic dispersions of several transition metals is promising for the visible light-induced water–cleavage reaction. Further development and study of conductive polymers and catalytic surface structure involving novel coordination metal complexes are in progress. A very high degree of stability and catalytic activity is produced; this provides encouragement for the potential application of catalytic conductive polymer films to practical photoelectrochemical devices for solar energy conversion. [1.7 FTE]

### *37. Basic Photoelectrochemistry Research*
*A.J. Nozik, J.A. Turner*

Basic research in photoelectrochemistry is conducted in (1) hot carrier effects, (2) superlattices and multiple quantum well photoelectrodes, and (3) colloidal and particulate semiconductors. Large quantization effects were found for the first time in photoelectrochemical systems using strained-layer and lattice-matched superlattice electrodes. The photocurrent spectra showed discrete peaks or steps that fitted very well to the theoretical energy-level structure of the GaAs quantum wells in the superlattices. For the strained-layer superlattice, photoelectron transfer from the discrete levels into the electrolyte is a hot carrier process. A theoretical model for electron transfer from superlattice photoelectrodes was developed that supported the hot electron transfer mechanism. Quantization effects in small particle semiconductor colloids of HgSe, PbSe, and CdSe were found to produce enhanced photoredox chemistry because of the increased band gap. [4.1 FTE]

# Chemical Physics

## Ames Laboratory
## Iowa State University
## Ames, Iowa 50011

### Fundamental Interactions Program $620,000

### *38. Statistical Mechanics of Nonequilibrium Systems*
*D.K. Hoffman*

New classical, semiclassical, and quantum mechanical scattering theories for inelastic and reactive collisions between gas-phase molecules are devised and implemented. This work provides powerful methods for investigating nonadiabatic and adiabatic reaction dynamics in systems of importance in combustion. These investigations are also incorporated into a statistical mechanical development of the kinetic theory of polyatomic gases in which transport, relaxation, and reactive processes are of interest. The dynamics and statistics of distributions of molecules adsorbed on surfaces under nonequilbrium conditions is analyzed via master equations. Such a theory is important for the appropriate interpretation of surface spectroscopic data associated with these processes. This project 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. These models for irreversible lattice processes are also applied to other (nonsurface) systems. [1.35 FTE]

### *39. Atomic, Molecular, and Free Radicals: Crossed Beam Kinetics*
*C.Y. Ng*

This project involves the study of the mechanisms and dynamics of fundamental processes that are relevant to combustion and plasma chemistry. Different experimental approaches combining the merits of the molecular beam method, photoionization and time-of-flight mass spectrometry, and laser spectroscopy are being developed in order to measure reaction cross sections of elementary chemical reactions at well-defined collision energies and internal states of the reactants and to identify the kinetic and internal energy distributions of the products. Research includes (1) high-resolution photoionization studies of hydrocarbon clusters and high-temperature vapors, (2) state-selected and state-to-state ion–molecule reactions (emphasizing charge exchange and proton transfer reactions), (3) vibrational relaxation of simple molecular ions, (4) laser photofragmentation spectroscopy of polyatomic molecules, and (5) neutral–neutral interactions by the crossed molecular beam method. [4.35 FTE]

### *40. Molecular Bonding Theory*
*K. Ruedenberg*

Properties of molecules such as geometric shapes, the behavior in electrical and magnetic fields, optical spectra, and in particular the energy changes that occur during chemical reactions are determined through quantum mechanical *ab initio* calculations of their electronic structures. Energy hypersurfaces that determine the course, directions, and rates of chemical reactions are mapped out as functions of atomic displacements, and their distinctive features are elucidated. Reaction energies, activation energies, transition states, and elusive intermediates are predicted. The electronic rearrangements that occur along reaction paths and their energetic and kinetic implications are analyzed. Fundamental theoretical and computational advances are made in many-electron quantum mechanics, including electron correlation, to establish practical methods for predicting reaction mechanisms with an accuracy that is useful to experimental chemists. Quantitative formulations of interpretative chemical concepts are developed and implemented by determining rigorous contributions of interatomic interactions to provide a reliable basis for the intuitive anticipation of difficult rigorous calculations. These methods are used to study oxidation–reduction reactions, exchange reactions, and isomerizations involving carbon, nitrogen, oxygen, hydrogen, and fluorine atoms. Of particular interest are reactions occurring in combustion, in the atmosphere, and during hydrogenations. [1.75 FTE]

## Argonne National Laboratory
## Argonne, Illinois 60439

**Chemistry Division** **$2,840,000**

### *41. Theoretical and Computational Chemistry*
*T. Dunning, Jr., R. Bair, M. Davis, L. Harding, R. Shepard, A. Wagner*

This project concentrates on theoretical studies of the energetics and dynamics of chemical reactions, emphasizing reactions of importance in the oxidation of hydrogen and simple hydrocarbon fuels. The main focus of the project is on calculation of accurate molecular interaction potentials, determination of the chemical dynamics on the computed (or other realistic) potential energy surfaces, and characterization of the molecular species (including ephemeral species) involved. Goals include the development of a qualitative understanding of the fundamental laws governing chemical reactivity and the development of quantitative techniques for calculating the energetics and dynamics of these elementary chemical processes. There is also a continuing effort devoted to developing the computational methodology needed to accurately predict the kinetics of chemical reactions. [11.4 FTE]

### *42. High-Resolution Spectroscopy and Intramolecular Dynamics*
*J.P. Hessler*

The project objective is to use high-resolution laser techniques to generate vacuum-ultraviolet light that is used (1) to study the complex dynamical processes needed to describe the behavior of excited polyatomic molecules and (2) to measure the kinetics of chemical reactions initiated by shock waves. To monitor dynamical processes, we excite specific predissociative and/or Rydberg states of polyatomic systems cooled by supersonic expansion techniques and monitor the temporal evolution of the system. Chemical reactions that evolve hydrogen or oxygen are studied in an ultrahigh purity shock tube. Rates of reactions and the absolute branching ratio of competing reactive channels are measured with our vacuum-ultraviolet laser flash absorption technique. [3.2 FTE]

### *43. Molecular Beam and Metal Cluster Chemistry Research*
*S.J. Riley, E.K. Parks, K. Liu*

The study of heterogeneous catalysis on a molecular level is pursued. Beams of catalytically active naked metal (nickel, chromium, vanadium, silver, copper, aluminum, iron) atom clusters containing two to several hundred atoms are generated by pulsed lasers, and their physical and chemical properties are characterized by laser-based, in-flight diagnostic techniques. Spectral and electronic properties are determined and experimental results are correlated with theoretical calculations. Mechanisms, energetics, and kinetics of cluster chemical reactions and of adsorption and catalytic processes on cluster surfaces are determined by the flow tube technique. The transient products are identified by laser ionization mass spectrometry. [10.3 FTE]

## Brookhaven National Laboratory
## Upton, Long Island, New York 11973

**Department of Applied Science** **$605,000**

### *44. Kinetics and Mechanisms of Alternative Fuels Combustion*
*R.B. Klemm, J.W. Sutherland*

The objectives of this project are (1) to measure absolute rate constants for elementary combustion-related reactions over a wide temperature range and (2) to investigate mechanistic factors involved in gas-phase combustion and pollutant formation processes. Emphasis is on alternative fuels that comprise a range of fuel types, including hydrogen, alcohols, and hydrocarbon synfuels. In pursuing the goals of this project, a facility has been developed that features experimental techniques including: (1) flash photolysis-resonance fluorescence (FP-RF); (2) discharge flow-resonance fluorescence (DF-RF); (3) flash photolysis-shock tube (FP-ST); and (4) discharge flow-photoionization mass spectrometry (DF-PIMS). The FP-RF and DF-RF methods are used to determine specific rates of elementary atom–molecule and radical–molecule reactions over a wide temperature span, ~200 to 1100 K. The recently developed FP-ST apparatus significantly extends the high-temperature capabilities for direct rate measurements. With this device, kinetic studies are performed over a temperature range from ~800 to 2000 K; and thus these measurements overlap the temperature range of the other, more conventional techniques used in this project. The DF-PIMS method is used for direct observations of reactants and products for elementary reactions to investigate the relevant reaction mechanisms. This DF-PIMS experiment uses the National Synchrotron Light Source. [6.0 FTE]

## Chemistry Department $2,650,000

### 45. *Theoretical Chemistry*
*S. Ehrenson, J.T. Muckerman, M.D. Newton*

The project objectives are to apply theoretical methods (1) to the study of energy flow in chemical reactions and (2) to the elucidation of molecular interactions involved in the storage and interconversion of energy in the gas phase and in condensed phases (including phenomena associated with charged species). Methods include (1) *ab initio* and semiempirical calculations of the energies and structures of molecules in specific electronic states and (2) classical and semiclassical treatments of the nuclear motion in kinetic processes involving these systems. Many of the techniques currently being developed and applied in this project play an important role in analyzing and interpreting experimental data obtained at the National Synchrotron Light Source (NSLS), the High Flux Beam Reactor (HFBR), and in other experimental programs in the Department. [5.7 FTE]

### 46. *Ion–Molecule Reactions with Applications to Fusion Energy Systems*
*L. Friedman, R.J. Beuhler*

A high-molecular-weight mass spectrometric facility has been developed that is capable of mass analysis and sensitive detection of singly charged ions with masses up to ~200,000. Ion source techniques have been developed for the generation of a wide variety of cluster ions with mass distributions by free jet expansion of weakly ionized plasmas. These techniques are used to investigate energy transfer in the impacts of cluster ions on solid surfaces. Electron microscopy is used to study morphology of craters and holes generated in thin target films by evaporation or sputtering processes that provide a channel of target cooling competitive with thermal conduction. The major goal of this project is to investigate the properties of the transient hot atom assemblies generated by cluster ion impacts. Practical applications of these impacts are also of interest and include their use to produce very small holes, to remove very thin layers of surface, and to alter the chemical architecture of the bombarded surface. In addition, cluster impacts provide a means of investigating a variety of high-temperature desorption phenomena. [5.9 FTE]

### 47. *Gas-Phase Photoionization and Photoelectron Spectroscopy of Molecules and Clusters*
*J.R. Grover, M. White*

The first objective of this project is to understand how molecules initially approach each other on the way to a reactive collision. Such understanding is necessary if accurate predictions of reaction rates are to be made. Measurements of the enthalpy of binding of van der Waals complexes and clusters of the reactive molecules are being made using the tunable, monochromatic radiation from the gas-phase beamline on the vacuum ultraviolet storage ring at the National Synchrotron Light Source. A subsidiary goal is to obtain previously unknown heats of formation for free radicals and molecular fragments that appear as reaction products or energetic reaction intermediates. The second objective is to explore and characterize the photoexcitation and subsequent ionization processes of resonantly excited molecules. A general photoelectron spectroscopy study of the ionization dynamics of neutral molecular ground and excited states using both synchrotron and laser radiation is under way. From the observed electronic and vibrational state distributions of the product ions, it is possible to investigate in detail the dynamics of the interaction between the anisotropic field of the molecular ion core and photoelectron. [4.4 FTE]

### 48. *Structure and Bonding of Solids and Molecules on Their Surfaces*
*J. Hrbek, T.K. Sham*

The main project objective is to improve the understanding of (1) the electronic interactions between surfaces and adsorbates and (2) the interactions among atoms in condensed matter, emphasizing technologically important materials. Identification of molecular structure of surface intermediates, active sites on surfaces, and the effect of promoters and poisons on surface selectivity and activity will make it possible to understand and control the chemistry of surfaces. These studies are being carried out through photoelectron spectroscopy, thermal desorption, electron diffraction, vibrational spectroscopy, and the development and application of synchrotron radiation spectroscopies (e.g., photoelectron and x-ray absorption, XANES, and EXAFS). Results of these studies are directly related to kinetic and mechanistic aspects of chemical reactivity and catalysis. [2.3 FTE]

### 49. *Chemical Crystallography*
*T.F. Koetzle, A. Kvick, R.K. McMullan*

Neutron and x-ray diffraction methods are used to solve significant problems in crystal and molecular structure. Emphasis is placed on structures where hydrogen and other light atoms are important and on disordered or partially ordered structures, since in these areas neutron diffraction, alone or in combination with x-ray diffraction, has unique advantages for determining molecular structure and investigating chemical bonding. In addition, access to the chemical crystallography beamline at the National Synchrotron Light Source will open up new areas for x-ray diffraction studies. Examples of systems investigated under the crystallography project include organometallic compounds, transition-metal hydrides, zeolites, fast-ion conductors, and dielectric materials. [5.2 FTE]

### 50. *Spectroscopy and Structure of Short-Lived Chemical Intermediates*
*T. Sears*

Studies of the structure and reactivity of molecular fragments are important to the understanding of gas-phase chemical reaction pathways and rates. Infrared laser techniques are applied to the study of these species, which are usually unstable and are present only in trace quantities in reaction mixtures. Analysis of the spectra will lead to details of molecular structure, intra- and intermolecular potential functions, and estimates of the concentrations of reaction intermediates involved in the course of reactions important in combustion and in semiconductor technology. [1.9 FTE]

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

### Applied Science Division $140,000

### *51. Combustion Chemistry*
*N.J. Brown*

Combustion chemistry consists of complex chain mechanisms involving radical species. The inherent difficulties encountered in high-temperature environments and the large number of species involved in hydrocarbon oxidation make the study of combustion chemistry difficult. One activity of the current research focuses on applying theoretical chemical kinetics to study high-temperature kinetics important in combustion. Emphasis is on investigating the dynamics of reactions using classical trajectories. Unimolecular and bimolecular reactions are investigated with realistic potential energy surfaces. Special emphasis is on elucidating the role of molecular angular momentum of intramolecular and intermolecular energy transfer processes. Rate coefficients for reactions important in combustion are also determined with statistical theories. Further activity concerns investigating the ignition chemistry of hydrocarbon–air mixtures. Identification of the principal elementary reaction steps that occur during ignition of hydrocarbon–air mixtures and determination of the corresponding rate coefficients are required to achieve an understanding of this phenomenon. Ignition will be investigated in a constant volume and steady-state system. Time-resolved evolution and decay of radical species will be monitored with a molecular beam mass spectrometer and by other spectroscopic methods. [1.8 FTE]

### Materials and Molecular Research Division $2,185,000

### *52. Energy Transfer and Structural Studies of Molecules on Surfaces*
*C.B. Harris*

The goal of this research is (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, 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 surface photoemission and the optical properties of thin films). [1.5 FTE]

### *53. Crossed Molecular Beams*
*Y.T. Lee*

The major focus of this research project is to elucidate detailed dynamics of simple elementary reactions that are theoretically important and (using the molecular beams method) to unravel the mechanism of complex chemical reactions or photochemical processes that play an important role in many macroscopic processes. Molecular beams of reactants are used to study individual encounters between molecules or to monitor photodissociation events in a collision-free environment. Most of the information is derived from measurement of the product fragment energy and angular distributions using a unique molecular beam apparatus designed for these purposes. Recent activities are centered on the following areas: (1) the direct probing of transition states of the $F + H_2$ reaction through the experimental observation of quantum mechanical resonance phenomena; (2) the mechanisms of elementary chemical reactions involving oxygen atoms with unsaturated hydrocarbons; (3) the dynamics of chemical reactions of electrochemically excited atoms; (4) the primary photochemical processes of polyatomic molecules, radicals, and ions; (5) intramolecular energy transfer of chemically activated and locally excited molecules using overtone excitation processes; and (6) the interaction potential of open shell atoms with rare gas atoms. [11.0 FTE]

### *54. Molecular Interactions*
*W.A. Lester, Jr.*

The project objective is to extend fundamental knowledge of the interactions and dynamics that govern energy transfer, reactive, and photodissociative molecular processes. The approach combines the use of potential energy surfaces constructed using rigorous nonempirical methods (*ab initio* Hartree-Fock, multiconfiguration Hartree-Fock (MCHF), and configuration interaction) with quantum, semi-, and quasi-classical approaches to nuclear dynamics. Current efforts focus on (1) single-photon photodissociation of $C_2N_2$ using *ab initio* MCHF potential energy surfaces and a recently developed adiabatic treatment of photodissociation dynamics; (2) extension of the adiabatic photodissociation development to bimolecular chemical reactions; (3) determination of cross sections for rotational and vibrational energy transfer by atom impact for electronically excited molecules ($He–H_2$, $HD(B^1\Sigma_u^+)$); and (4) the application of Monte Carlo methods to the computation of potential energy surfaces and properties of individual molecules. [5.5 FTE]

### *55. Theory of Atomic and Molecular Collision Processes*
*W.H. Miller*

This research is primarily involved with the development of theoretical methods and models for describing atomic and molecular collision processes. Specific topics of interest include the theory of inelastic and reactive scattering, collision processes involving electronically excited atoms or molecules, collisional ionization phenomena, statistical theories of chemical reactions, scattering of atoms and molecules from surfaces, and the interactions of molecular systems with high-power laser radiation. Much of this research is involved with the development and application of a general semiclassical mechanics that allows combination of classical mechanics and quantum mechanics in a correct and useful manner. This has been extremely successful in providing an understanding of the various quantum effects that are seen in molecular phenomena, and it also often provides simpler computational methods for quantitative calculations. Certain research topics are more amenable to a completely quantum mechanical approach, and these sorts of theoretical techniques are also used. The ability to understand, and thus to model and to predict, chemical kinetics phenomena in the gas phase has widespread practical importance in a number of different areas. Among these are atmospheric chemistry and physics, interactions of molecules with strong laser fields, and energy transfer and chemical reactions in flames and combustion. [3.2 FTE]

### *56. Selective Photochemistry*

*C.B. Moore*

The fundamental goals of this project are to understand the photophysics of selective excitation of molecules, the dynamics of energy transfer and specificity loss, and the chemical reactions of excited states. The nature of the energy states of molecules as a function of excitation energy and of molecular size and structure determines the intramolecular flow of energy. The spectra of vibrationally excited molecules are studied by laser-based methods in order to determine the strength of coupling of one vibrational mode to another and to elucidate the rates and sequences of energy flow among all modes of an excited molecule. Unimolecular reaction rates are measured. An understanding of the competition between energy transfer and unimolecular reaction as a function of excitation energy, molecular size, and chemical constitution is sought. The mechanism and selectivity of bimolecular reaction processes is often revealed by the dependence of reaction rates on quantum state, isotopic substitution, and temperature. Many photochemical and combustion processes involve the formation of short-lived reaction intermediates or collision complexes. Laser flash kinetic spectroscopy is used to identify transient species and measure their reaction rates. The results are useful in the modeling of combustion processes and of photochemical reactions such as C–H bond activation by organometallic photoproducts. [4.3 FTE]

### *57. 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. Primary emphasis will be on ionized systems, electrolyte solutions, and plasmas. Systems comprising fused salts mixed in any proportion with water are being studied experimentally and with semiempirical theory. Recently the critical points for pure NaCl and KCl were predicted from a combination of rigorous statistical thermodynamics (for the vapor) and an extrapolation of the empirical equations (for the liquids). With guidance from corresponding states theory, a fused salt–polar liquid system was discovered with a critical point at 140°C where detailed laboratory study is feasible. 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 included relativistic quantum mechanical methods for calculating energies, bond distances, and other properties of the ground and excited states of molecules containing very heavy atoms where the conventional nonrelativistic methods are inadequate. Such results are important in evaluating possible laser systems and for models of catalytic entities including heavy atoms (e.g., platinum). [2.2 FTE]

### *58. Far-Infrared Laser Spectroscopy of Reaction Intermediates*

*R.J. Saykally*

Sophisticated far-infrared laser techniques are combined with laser photolysis and supersonic beam technology for the study of spectra, structures, potential surfaces, and dynamics of molecules that are intermediates in chemical reactions. Anisotropic bimolecular potential energy surfaces are obtained from the direct measurement of vibration-rotation spectra of van der Waals bonds in molecular complexes. Both nonreactive (e.g., Ar–HCl) and reactive (e.g., F–HF) bimolecular systems are studied. This work complements the measurement of bimolecular potential surfaces by molecular beam scattering experiments. The structures and dynamics of molecular complexes are also studied as a route to understanding the dynamical properties of condensed phases. [4.5 FTE]

### *59. Potential Energy Surfaces for Chemical Reactions*

*H.F. Schaefer, III*

This research project has two goals, related yet distinct. The first goal is the development of new theoretical and/or computational methods for describing what electrons do in molecules. The single outstanding problem in the field is the correlation problem, that of formulating models for going beyond the single-particle or Hartree-Fock approximation. The second goal is to apply these theoretical methods to significant problems of broad chemical interest: (1) model theoretical studies of chemisorption, metal clusters, and organometallic species; and (2) potential energy surfaces that govern gas-phase chemical reactions. Research in the former area is ultimately aimed at a truly molecular understanding of catalysis, a subject pertinent to future energy requirements, but sometimes approached by trial and error methods. In the latter area, research sometimes tends toward molecules potentially important in combustion or atmospheric chemistry and the development of high-power laser systems. Theoretical chemistry has become a significant source not only of broad generalities, but also of specific predictions concerning molecular systems that may be very important, but inaccessible to experiment. [5.0 FTE]

### *60. Photoelectron Spectroscopy*

*D.A. Shirley*

The major project objective is to conduct exploratory research on the interaction of vacuum ultraviolet and soft x-ray radiation with matter, emphasizing synchrotron radiation and photoelectron spectroscopy. The project also supports the national programs through innovation and development of new experimental methods based on synchrotron radiation in the energy range 10 to 4000 eV, and through the training of doctoral candidates in the use of synchrotron radiation. The reaction of radiation in this energy range with matter yields (as one reaction product) an unbound electron in a highly excited final state. The further interaction of this electron with the other reaction product(s) can provide unique and definitive information about both reactants and products. Focus is on (1) understanding of electron correlation in atoms and small molecules, including the characterization of continuum resonances and correlation satellites, and (2) characterization of the atomic and electronic structure of surfaces. This includes both structural studies by photoelectron diffraction (ARPEFS) and electronic structure determinations on and near the surface. Related supportive research includes photoelectron spectroscopy in molecular beams and high-resolution electron energy loss spectroscopy on surfaces. [11.5 FTE]

## Lawrence Livermore National Laboratory
## Livermore, California 94550

### Division of Chemical Engineering $38,000

### *61. Chemical Kinetics Modeling*
*C.K. Westbrook*

This project focuses on computer modeling of chemical kinetics of combustion in laboratory and practical systems. Particular emphasis is placed on hydrocarbon fuels that are widely used in present combustion devices. Construction and validation of comprehensive reaction mechanisms for these fuels will identify those elementary reactions on which the computed results are most dependent and, therefore, merit the closest attention from experimental and theoretical research. Experimental data from shock tubes, plug flow reactors, stirred reactors, laminar flames, and detonations are used to test and validate the reaction mechanisms. Fuels to be examined include n-pentane, n-octane, isooctane, ethanol, and propionaldehyde. Once the reaction mechanisms have been validated thoroughly, they are used to examine the role of chemical kinetics in practical combustion systems. Past applications have considered heat transfer and unburned hydrocarbon emissions from automobile engines, kinetic inhibition of flames and detonations, and the influence of pressure on combustion rates. Applications in progress include the kinetics of engine knock in internal combustion engines, kinetics of cool flames and multistage ignition, and the influence of pressure on combustion rates. Applications in progress include the kinetics of engine knock in internal combustion engines, kinetics of cool flames and multistage ignition, and the influence of fuel molecular structure on various combustion parameters. [0.3 FTE]

## Oak Ridge National Laboratory
## Oak Ridge, Tennessee 37831

### Chemistry Division $350,000

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

The project studies the photoelectron dynamics of molecules and metal vapors using angle-resolved photoelectron spectroscopy and synchrotron radiation. Phenomena investigated include: (1) the Cooper minimum, (2) shape resonances, (3) autoionization, (4) correlation satellites, (5) interchannel coupling, and (6) near-threshold behavior of core shells. Systematic studies are pursued on the chloromethanes, iodine-containing molecules, benzene, triatomic molecules, transition metal compounds, and various metal vapors including silver, gallium, lead, and some 3d transition metal elements. Supportive calculations using the multiple-scattering X$\alpha$ method are performed and correlated with observed cross sections and angular distribtion parameters. Improved computer handling of the experiment allows the introduction of constant-ionic-state techniques. Besides providing fundamental information in atomic and molecular science, the project supplies data and ideas for studying molecules adsorbed on surfaces, clarification for solid-state properties in metals, and an understanding of clusters. [2.2 FTE]

## Sandia National Laboratories
## Livermore, California 94550

### Combustion Research Facility $5,170,000

### *63. Flame Dynamics Research*
*R. Cattolica, W. Flower, S. Johnston*

The purpose of this research is to investigate the spatial and temporal interactions between chemical species, temperature, and fluid motion as they occur in flames. Included are the dynamics of carbonaceous particulates in sooting flames and the ignition, free propagation, and quenching of transient gas-phase flames. An important aspect includes the development and application to flames of advanced optical diagnostics such as time-resolved, planar, laser-induced fluorescence and diffusion-broadening spectroscopy. Fluorescence imaging has been used to study the chemical structure of a laminar flame interacting with a vortex ring. The time-dependent generation and evolution of the OH molecule during the interaction was observed. Comparison of these results with the modeling predictions generated using the vortex dynamics computational method has been made. Soot size and number density, and the effect of increasing pressure on these quantities, have been determined in a laminar diffusion flame. Local soot formation rates have been determined in laminar diffusion flames using laser-velocimetry flow-field measurements and light-scattering measurements of soot concentration. Species thought to be responsible for soot particle surface growth have been detected using coherent anti-Stokes Raman spectroscopy. The quantity of soot emitted by a flame is determined by a competition between soot formation and soot oxidation. Measurements of integrated soot volumes at pressures up to 10 atm were used to determine how the relative roles of soot formation and oxidation processes are affected by pressure. [2.0 FTE]

### *64. Turbulent Reacting Flow Research*
*R. Dibble, R. Schefer, S. Johnston*

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 this understanding to improve predictive capabilities for turbulent combustion. A new laboratory incorporating a vertical flame tunnel (and making use of the Combustion Research Facility dye laser) is fully operational. Multispecies Raman concentration and temperature measurements, combined with simultaneous velocity determinations, have been compared with model predictions to estimate the influence of chemical nonequilbrium on mean turbulent flame quantities. One- and two-dimensional imaging of major and minor species is producing new insight into mechanisms of local flamelet burning and extinction. A chemically reacting turbulent flow cooperative group comprised of participants from private industry, universities, and Sandia National Laboratories has been formed and meets on a regular basis. [3.0 FTE]

### 65. *Combustion Research Facility (CRF) Operations and Visiting Scientist Support*
*G. Drummond*

This project provides for the operation of the Combustion Research Facility (CRF) and sustains the visitor support program, which includes staff effort in support of visitors, transfer of CRF-developed technology, and the provision of administrative, computer (time, codes, and software development), and other support of visiting researchers. Staff is provided for all categories of visits, from one-day scientific discussions, to extended periods of long-term collaborative research. Transfer of technology developed at the CRF to interested industries, universities, and government laboratories is effected through "short courses", a vigorous postdoctoral program, research reports, technical presentations, and various periodic publications. [9.0 FTE]

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

This project aims at developing coherent Raman diagnostic techniques in support of CRF programs. Detailed studies are made of the significance of several factors for experiments using CARS, a leading technique for time-resolved measurements of temperature and major species concentrations. These factors include laser photon statistics, Stark effects, laser lineshape convolutions, *in situ* normalization, and interferences between resonant Raman and nonresonant background contributions. A new, high-resolution CARS system is used to examine saturation (another consideration when analyzing CARS measurements) and to determine nonresonant backgrounds of fuel molecules. The modification of CARS spectra at high pressure due to 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. [5.0 FTE]

### 67. *Flame Chemistry: Modeling and Experiments*
*G.A. Fisk, J.A. Miller, R.J. Kee, L.R. Thorne, D.W. Chandler*

The principal objective of this research is development of comprehensive models for the chemical processes that govern flames. Emphasis is on production and destruction of pollutants in flames. New numerical techniques have been implemented to provide fast and accurate methods for solving the one- and two-dimensional laminar flame equations (including sensitivity analyses), thereby facilitating comparisons with a wide range of experimental results. Laboratory studies emphasize the use of advanced laser probes for measurements of radical and stable species concentration profiles in flames. Other techniques, including molecular beam-mass spectrometry and Fourier transform infrared spectroscopy, are also employed. Recent work has determined the extent to which a molecular-beam-sampling probe perturbs the structure of one-dimensional flames. Experiments and related modeling have established the detailed mechanism whereby fuel-bound nitrogen is converted to NO in flames, and the mechanism through which NO can be converted to other species. [4.0 FTE]

### 68. *Chemical Kinetics and Dynamics*
*G.A. Fisk, F.P. Tully, R.A. Perry, D.W. Chandler, C. Melius, J.A. Miller*

This research is directed at understanding fundamental chemical processes of importance in combustion. Laser photolysis is used to produce radicals in slow-flow reactors, and the kinetics and mechanisms of ensuing radical–molecule reactions are followed by laser-induced fluorescence. Laser photoexcitation is used to produce energetic and reactive molecules whose subsequent chemistry (relaxation and reaction) is followed in time via state-specific detection of products. Theoretical methods are used to analyze pathways of combustion reactions. BAC-MP4 (bond-additivity-corrected fourth-order Moller-Plesset perturbation theory) calculations are used to determine the properties of stationary points (stable molecules and saddle points or transition states) on the potential energy surfaces of critical reactions. Statistical methods are used to predict rate coefficients and branching ratios from this potential surface information. In addition, the influence of inter- and intramolecular energy transfer on unimolecular reactions is studied using dynamical methods. Recent experimental work has emphasized the reactions of OH and NCO radicals with hydrocarbons, and the rotational relaxation of vibrationally excited hydrogen. Recent theoretical work has calculated rate constants for reactions such as O + HCN, OH + HCN, and O + OH. [4.0 FTE]

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

This project supports development of new nonlinear laser-based techniques for detecting trace species in combustion environments, and theoretical studies in support of CRF projects. In the first area, detailed studies of two-photon-excited fluorescence detection of OH in flames have been made. Results from these studies have been compared to experiments on OH detection using one-photon-excited fluorescence. The ultraviolet absorption spectrum of hot $O_2$ in flames has been characterized. Profiles of OH and hydrogen atoms in sooting and nearly sooting rich flames have been performed. Photochemical effects in measurements of H and O atoms in flames have been observed. In the area of theoretical studies, collisional narrowing of $N_2$ and CO has been modeled both by semiclassical scattering calculations and by simple scaling theories based on fits to experimental data. Analytic theories have been developed to explain saturation and ac Stark effects observed in multiphoton fluorescence experiments on atomic hydrogen. [4.0 FTE]

### 70. *Combustion Research Facility (CRF) Central Laser Systems*
*R.L. Schmitt, R.L. Farrow, L.A. Rahn, R.E. Palmer*

This project includes the continued development of existing CRF central lasers and research in support of future major laser systems. 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-dimensional imaging of turbulent nonpremixed flames. A multipurpose laser system (Sirius) consists of a frequency-doubled Nd:YAG laser and several dye laser options, including a broad-band dye 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. Present laser research in support of advanced central lasers includes diode-laser injection locking of Nd:YAG lasers for stable single-axial-mode operation, and studies of advanced dye laser design. [3.0 FTE]

# Atomic Physics

## Argonne National Laboratory
## Argonne, Illinois 60439

**Physics Division** **$1,883,000**

### 71. *Photoionization Mass Spectrometry, Photoelectron Spectroscopy, and Photodissociation*
*J. Berkowitz*

Fundamental processes in the photoionization of atoms and small molecules are studied in the vacuum ultraviolet at high photon resolution. For molecules, alternative decomposition modes are investigated to provide important thermochemical values, structural, and dynamical information. Photoelectron spectroscopy is focused on the more difficult high-temperature vapor species and reveals their detailed electronic structure. A recently completed apparatus enables us to study directly the spectroscopy and dynamics of molecular-ion decomposition by analyzing the decomposition products from interaction of ultraviolet laser radiation with selected molecular ions. [4.5 FTE]

### 72. *Atomic Spectroscopy with Fast Beams at Argonne National Laboratory (ANL)*
*H.G. Berry, L. Young*

Atomic structure studies using fast-ion beams are aimed principally at improving understanding of relativistic and quantum-electronic effects in heavy ions. Systems with only a few (1 to 4) electrons are studied to test precise *ab initio* calculations; many-electron systems are studied to test more general relativistic calculations (e.g., relativistic Hartree-Fock). In atomic collision studies, the alignment and orientation production of excited states in fast-ion–solid interactions are analyzed. Total excitation probabilities are also measured and studied in terms of secondary-electron production and molecular coherence effects. Optical techniques are used to study the dynamics of fast and atomic ions in solids and at surfaces. Resonant laser excitation of fast ions is being used to study (in detail) relativistic fine structures and hyperfine structures of both positive and negative ions of low nuclear charge. Research includes use of lasers operating in the ultraviolet. [5.8 FTE]

### 73. *High-Resolution Laser-RF Spectroscopy with Atomic and Molecular Beams*
*W.J. Childs, L.S. Goodman*

This project is directed toward a detailed understanding of the structure of atoms and small molecules. In the recent past the spin-rotation and hyperfine interactions of alkaline-earth monohalide radicals have been systematically studied and their dependence on vibrational, rotational, and isotopic effects elucidated. The experimental methods have now been extended to make possible measurement of the electric-dipole moments of such radicals. A similar project aimed at a systematic understanding of the hyperfine interaction throughout the 4f-shell of the rare-earth atoms is progressing concurrently. A new apparatus for analogous studies of atomic and molecular ions using collinear laser and radiofrequency spectroscopy is under development. [3.6 FTE]

### 74. *Interactions of Fast Atomic and Molecular Ions with Solid and Gaseous Targets*
*E.P. Kanter, Z. Vager, D.S. Gemmell*

Argonne National Laboratory's 4.5-MV Dynamitron accelerator is used to study the interactions of fast (MeV) atomic and molecular ions with matter. A unique feature is the exceptionally high resolution ($\sim 0.005^\circ$ and $\sim 300$ eV) in angle and energy obtained in detecting particles emerging from the target. The accelerator currently permits the coincident detection of up to three molecular dissociation fragments with conventional discrete particle detectors. A new multiparticle-imaging detector system has been developed to allow detection of multiparticle events consisting of up to eight particles. 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 (i.e., each molecular ion incident upon a solid target forms a tight cluster of atomic ions that remain correlated in space and time as they penetrate the target). Additionally, these techniques allow direct determination of the geometrical structures of molecular ions entering the target. [5.2 FTE]

## Brookhaven National Laboratory
## Upton, Long Island, New York 11973

**Department of Applied Science** **$248,000**

### 75. *Atomic Physics Research*
*K.W. Jones, B.M. Johnson*

Studies of the physics of multiply charged heavy ions are made with synchrotron radiation from the Brookhaven National Synchrotron Light Source (NSLS) and heavy-ion beams from the Brookhaven Tandem Accel-Decel Laboratory (TADL). A dedicated atomic physics station on the X-26C beam line at the NSLS x-ray ring is used for experiments with white or monochromatic x rays. An extended study of the K-shell photoionization of argon produced by filtered white radiation is in progress. Measurements of the charge states and fluorescent radiation and the development of methods for trapping the ions in Penning- and Kingdon-type ion traps are the initial points of interest. The trapped argon ions are used as targets for sequential photoionization to produce mean charge states greater than those found for a single ionization event. The ions can also be extracted from the trap for subsequent use in ion–atom collision experiments. Equipment for crossed photon-ion beam experiments is being developed using a standard ion source. Inner-shell vacancy processes, charge transfer, and equilibrium charge states in ion–gas collisions are studied with negative ions and with positive ions produced by the tandem accel-decel method. [3.0 FTE]

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

**Materials and Molecular Research Division** **$233,000**

### 76. *High Energy Atomic Physics*
*H.A. Gould*

The goal of this project is to understand atomic collisions of relativistic ions and to test quantum electrodymanics (QED) in atoms of very high atomic number (Z). These are new areas of research that involve physics not accessible at lower energies or with lower-Z ions. Recent results include detailed measurements of cross sections for electron capture in the K shell and higher shells of relativistic zenon ($Z=54$) and ionization of K shell electrons of relativistic xenon. These and earlier measurements in this project have led to an understanding of relativistic heavy-ion–atom collisions that, in many cases, is now more complete than for nonrelativistic collisions. Present activities include: (1) measurement of ionization of L- and M-shell electrons of relativistic uranium, (2) multiple electron capture and ionization, and (3) (as a test of the higher order terms in the QED self energy) a measurement of the $1s2p\ {}^3P_0$ lifetime in helium-like uranium ($Z=92$). Future experiments will explore a new mechanism for electron capture; capture from electron–positron pairs produced by relativistic ion–atom collisions. Other experiments will examine relativistic heavy-ion–electron collisions, and channeling and polarization of relativistic heavy ions. [2.0 FTE]

### 77. *Atomic Physics*
*M.A. Prior*

The Lawrence Berkeley Laboratory (LBL)/Materials and Molecular Research Division low-energy atomic physics program is devoted to experimental studies of collisions and spectroscopy in simple atomic systems. Emphasis is on topics that challenge current atomic theory, and have relevance to processes present in controlled thermonuclear, astrophysical, and laser plasmas. Examples of such studies include (1) electron-capture collisions by low-energy multiply charged ions; (2) precision x-ray spectroscopy of hydrogen-, helium-, and lithium-like ions of high atomic number (Z); and (3) the measurement of forbidden line spectra and decay rates (or lifetimes) of metastable ions. These studies have produced important tests of quantum electrodynamic and relativistic effects in ions of high Z. The approach takes advantage of unique facilities and expertise available at LBL or developed within the research program. Current effort develops and utilizes facilities that make available low-energy, multiply charged ion beams from the LBL/ECR ion source for atomic physics research. In this program, a laser spectroscopic measurement of fine structure in four-electron $Ar^{14+}$ is under way, and planned projects include studies of the polarization and spectroscopy of recombination radiation following electron capture, and electron excitation of multiply charged ion targets of relevance to x-ray laser systems. [1.6 FTE]

## Oak Ridge National Laboratory
## Oak Ridge, Tennessee 37831

**Physics Division** **$2,382,000**

### 78. *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. Recent activities include calculations of multiple K-, L-, and M-shell vacancy production by ions (being detected in x-ray satellites at the Oak Ridge National Laboratory Holifield heavy-ion accelerator), subshell vacancy production including the effects of vacancy rearrangement processes, multiple vacancy production in coincidence with the final projectile charge (to separate capture from noncapture events), coincident excitation and ionization, electron ejection and positron production in collisions of very heavy ions with very heavy atoms, and collisions of ions with atoms containing a highly excited (Rydberg) electron. New 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. Computer programs for solution of the time-dependent many-electron Hartree-Fock and one-electron Dirac equations have been developed. [1.0 FTE]

### 79. *Accelerator Atomic Physics*
*S. Datz, P.F. Dittner, P.D. Miller, H.F. Krause*

The project objective is to achieve a detailed understanding of the interactions of high-energy, multiply charged ions with gas and solid targets, with electrons, and with photons, both with and without external applied fields. The primary facility used is the EN-tandem accelerator, and in recent years some experiments have also involved the Holifield Heavy Ion Research Facility. A very active program of high-resolution, zero-degree projectile Auger electron spectroscopy has been pursued. For example, when collisions of 2.5 to 3.5 MeV $C^{3+}$ with a helium target were used to populate $1s^22pn^{\ell}$ states of berylium-like $C^{2+}$, overlapping states of opposite parity within a given n-manifold were observed to produce surprisingly large forward-backward asymmetries of their Auger decay electrons. Projectile n- and $\ell$-distributions were measured for Auger electrons from doubly excited states populated by collisions with gas and solid targets. Resonant Transfer and Excitation (RTE) to discrete bound states were observed for lithium-like $O^{5+}$ incident on a helium target. A new technique was developed for measuring the metastable content of berylium-like and boron-like oxygen- and carbon-ion beams. Cross section measurements of dielectronic recombination for all available lithium-like, berylium-like, boron-like, and sodium-like ions have been completed using merged beams of electrons and multiply charged heavy ions. Mechanisms for transfer ionization, in highly charged ion–helium collisions (e.g., $U^{30+}$ at 120 MeV) have been investigated. Monte Carlo calculations of resonant coherent excitation of one electron ions moving in crystalline channels have continued. The Accelerator Atomic Physics group has also been active during the last year in defining design criteria for a Heavy Ion Storage Ring for Atomic Physics (HISTRAP). [5.6 FTE]

### *80. EN Tandem Operations*

*P.D. Miller, P.L. Pepmiller*

The EN-tandem Van de Graaff is operated for atomic physics research. Terminal voltages up to 6.0 MV are routinely achieved, and ions of all elements with $Z < 9$, as well as many heavier ions are available to users. The user group includes members of the physics division, other divisions at Oak Ridge National Laboratory, faculty and students from various universities, and representatives from industry. A VAX-750/CAMAC-based data acquisition system is available to users. Recent major beam usage has included: Auger electron spectroscopy of multiply charged projectile ions, two-electron correlated electron transfer studies, convoy electron studies, angular distributions of low-energy recoil ions, trapping of low-energy highly charged ions, and dielectronic recombination of multiply charged ions interacting with a merged beam of electrons. [1.3 FTE]

### *81. Collisions of Low-Energy Multiply Charged Ions*

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

This experimental project is aimed at improving our understanding of inelastic collision processes involving multiply charged ions with atoms and molecules at the lowest attainable collision energies. Current emphasis is on measurement of total cross sections for electron capture by highly stripped ions from hydrogen atoms at energies below 1 keV/amu. Toward this end, two different experimental approaches are being pursued. The recently constructed Oak Ridge National Laboratory-ECR ion source was used as a source of low-energy, highly stripped ions to study charge exchange reactions at low energies. An ion–atom merged-beams apparatus was used with the ECR ion source to study such collisions at center-of-mass energies in the eV/amu range, where theoretical predictions of increasing cross sections with decreasing energy remain untested. Experiments have also been initiated to measure the energy distribution of electrons ejected in glancing collisions of slow, highly charged ions with a solid surface. [1.2 FTE]

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

**Laser and Physical Chemistry Department-1124** **$147,000**

### *82. Atomic Processes*

*A. Owyoung, A.V. Smith*

The goal of this project is to develop techniques for more efficient production of vacuum ultraviolet light by means of nonlinear optical frequency mixing. Present investigations focus on using two-photon resonant sum frequency mixing in atomic mercury vapor, particularly for generation of coherent light in the 130 nm region. For this purpose a number of spectroscopic parameters in mercury, of importance for frequency mixing, are measured. These measurements include molecular absorption as well as a large number of f values for which we have devised new and more accurate nonlinear optical methods of measurement. This information will make it possible to calculate and optimize conversion efficiencies in a systematic fashion for the first time. Results obtained show that efficiencies several orders of magnitude greater than those demonstrated so far are possible. The role of higher order nonlinear processes in improving mixing efficiencies is studied. For example, we have demonstrated that fifth-order mixing can dominate under some conditions and that intensity-dependent refractive indicies can allow conversion in spectral regions where it is not normally allowed. We have also proposed that induced structure in the ionization continuum can enhance conversion efficiency. [1.5 FTE]

# Chemical Energy

## Ames Laboratory
## Iowa State University
## Ames, Iowa 50011

**Processes and Techniques Program** **$912,000**

### *83. Organometallic Complexes in Homogeneous Catalysis*

*R.J. Angelici*

Although sulfur is removed commercially from thiophenes in crude petroleum by hydrodesulfurization (HDS) over sulfided metal catalysts, the mechanistic details of this process are not understood. The purpose of this project is to develop some understanding of the reactivity of thiophene coordinated to transition metals as might occur on the catalyst surface. It has been found that the $\pi$-complexed thiophene in $(\eta\text{-}C_4H_4S)Mn(CO)_3^+$ and $(\eta\text{-}C_4H_4S)Ru(\eta\text{-}C_5H_5)^+$ are highly activated to react with model surface species such as hydrides and sulfides. Reaction with acids leads to the formation of 2,3-dihydrothiophene, a possible intermediate in the HDS process. Reactivity studies of 2,3-dihydrothiophene to determine how sulfur is removed from this molecule are also in progress. These studies are offering new mechanistic pathways by which the HDS process might occur. [3.0 FTE]

### *84. Chemical Kinetics and Reactivity of Transition Metal Complexes*

*J.H. Espenson*

The primary objective is to provide fundamental data on chemical reactivity bearing on chemical reactions involved in homogeneous catalysis, synthetic fuels, the Fischer-Tropsch process, and the control of acid rain. The principal approach is based on the study of chemical kinetics and reaction mechanisms using a wide variety of experimental techniques applied to reactions occurring from microseconds to days or longer. The reactions under investigation include spontaneous and induced decomposition, heterolytic and homolytic metal–carbon bond cleavage (and the associated bond-dissociation energies), radical-induced electron transfer, free-radical displacement, alkyl transfer, and insertion into metal–metal and metal–carbon bonds. The chemical entities under study include organometallic derivatives of cobalt, chromium, nickel, and rhodium; dinuclear complexes of platinum, nitrogen oxides, and oxoacids; sulfur dioxide; and molecular elements (e.g., $S_8$ and $P_4$). [3.8 FTE]

### *85. Nuclear Magnetic Resonance (NMR) Studies of Coals, Catalysts, and Amorphous Semiconductors*
*B.C. Gerstein*

Nuclear spin dynamics are used to probe the physics and chemistry of materials involved in heterogeneous catalysis, coals and coal products, and materials science. Examples include precursor pitches used in electrodes for aluminum production, zeolitic catalysts used in conversion of methanol to ethylene, bimetallic catalysts, heavy metal halide cluster compounds, and amorphous semiconductors used in photoconversion. [3.0 FTE]

### *86. Fundamental Investigations of Supported Bimetallic Catalysts*
*T.S. King*

This project combines high-resolution solid-state transient NMR techniques with more traditional experimental techniques to examine the nature of supported bimetallic catalysts. This project investigates these catalysts by: (1) determining the state of the metal atoms under reaction conditions, (2) determining the nature of adsorbed species, (3) investigating the chemisorption behavior of simple molecules, and (4) characterizing the catalytic activity and selectivity of model reactions as a function of the state of the catalyst and adsorbed species. [0.6 FTE]

### *87. Spectroscopic and Kinetic Characterization of Metal Oxide and Sulfide Catalysts*
*G.L. Schrader*

The goal of this research is to develop a fundamental understanding of the solid-state and surface chemistry of heterogeneous catalysts and the mechanisms of catalytic reactions. Metal oxide and sulfide catalysts that can be used to produce synthetic fuels or to hydrotreat coal-derived liquids are being investigated. Catalysts for energy-efficient routes to specific chemicals are also included. Laser Raman spectroscopy and Fourier transform infrared spectroscopy are being developed for use in the characterization of catalysts and adsorbed species. *In situ* experiments are conducted involving functioning catalysts; simultaneous spectroscopic and kinetic measurements can be performed at the temperatures and pressures typical of industrial operating conditions. These techniques provide a direct method for relating catalyst structure and composition to activity and selectivity. [2.9 FTE]

### *88. High-Temperature Gas-Phase Pyrolysis of Organic Compounds*
*W.S. Trahanovsky*

This research aims at understanding the fundamental thermal reactions of organic compounds, especially those that could be important in the pyrolysis of coal and coal-derived liquids. Study includes (1) preparation of specific reactive molecules thought to be intermediates in pyrolysis reactions and investigation of their spectroscopic and chemical characteristics and (2) reactions thought to involve certain reactive molecules as intermediates. Most pyrolyses are carried out using the flash vacuum pyrolysis technique. Much of the work concentrates on (1) pyrolysis reactions thought to involve quinodimethanes as intermediates, (2) preparing and characterizing these and related species, and (3) thermal reactions of these species and products derived from them. Effort is being focused on the development of flow and low-temperature solid-state NMR techniques to obtain the NMR spectra of reactive molecules such as ortho-quinodimethanes. Specific reactive molecules under study include ortho-quinodimethanes derived from benzenes, naphthalenes, furans, and thiophenes. [2.5 FTE]

## Argonne National Laboratory
## Argonne, Illinois 60439

### Chemical Technology Division $522,000

### *89. Fluid Catalysis*
*J.W. Rathke, M.J. Chen, R.J. Klingler*

This research is designed to explore catalysis mechanisms in the areas of homogeneous catalytic hydrogenation and catalytic odixation chemistry. Currently under investigation are the mechanisms by which metal oxides promote carbon monoxide and carbon dioxide hydrogenation. Fundamental equilibrium processes that relate hydrogen, steam, carbon monoxide, and carbon dioxide pressures to concentrations of reactive formate, hydride, hydroxide, oxymethylene, and oxide species in a soluble system have been identified. These processes occur in concert, and together complete cycles for methanol synthesis and water–gas shifting using soluble oxide complexes. Also investigated are mechanisms and theory associated with electron transfer processes that occur in the catalytic aerobic oxidations of organic bases. The new chemistry is investigated using high-pressure kinetic techniques combined with spectroscopic and theoretical (molecular orbital) methods. [3.8 FTE]

### Chemistry Division $1,993,000

### *90. Inorganic Fluorine Chemistry*
*E.H. Appelman, L. Stein*

This project is directed toward (1) the synthesis and characterization of novel and aggressive 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. It is also concerned with the use of the techniques of inorganic fluorine chemistry to prepare new compounds of the actinide elements in their highest oxidation states. A separate but related aspect of the project deals with the chemistry of the radon fluorides. Efforts include a study of the mechanism of production $OF_2$ in the reaction of fluorine with aqueous solutions, an attempt to synthesize a simple oxide fluoride of neptunium(VII), and a study of the silver(I)-mediated reaction of selected hypofluorites with organic substrates. The ion exchange behavior of radon fluorides on selected oxidation-resistant ion-exchange materials is being studied in the radon chemistry subprogram to determine the precise nature of radon fluorides in nonaqueous solutions. [1.5 FTE]

### *91. Premium Coal Sample Program*
*K.S. Vorres*

The objective of this program is to provide the U.S. basic coal science research community with long-term supplies of a small number of premium coal samples. The premium coal samples produced and distributed by this program are as chemically and physically identical as possible, have well-characterized chemical and physical properties, and must be stable over long periods of time. Coals are mined, transported, processed into desired particle and sample sizes, and packaged in environments that are as free of oxygen as possible and that maintain the natural moisture content to ensure that the coals are kept in as pristine and stable a condition as possible. These premium samples will be distributed to researchers upon request. A computer data base will be included in this program to provide researchers with easy access to detailed information on sample availability, the physical and chemical properties of the coals, and references to the results of research obtained using these samples. [4.9 FTE]

### 92. *Separation of Coal Macerals*

*R.E. Winans, G.R. Dyrkacz, C.A.A. Bloomquist*

This project seeks to reduce the complexity of coal science by developing new methods for separating and characterizing coal macerals. The density gradient centrifugation technique developed in this study has provided pure maceral samples for fundamental coal research and samples for the study of coal maceral characteristics, which could lead to improved separation methods. The project focuses on investigating surface properties of macerals with radiolabeling, proton NMR, FTIR, and microcalorimetry to provide information that will be used in improved separation methods. [2.5 FTE]

### 93. *Characterization and Reactivity of Coals and Coal Macerals*

*R.E. Winans, R. Hayatsu, R.E. Botto, R.G. Scott, R.M. McBeth*

The major objective of this project is to elucidate the micro- and macrostructure of coal macerals and the Argonne Premium Coal Samples. This information will be correlated with the chemical, thermal, and biological reactivity of these substances. Our approach combines selective chemical modification and degradation with a number of instrumental techniques. In addition, realistic coal models are being synthesized from presumed coal precursors, yielding information on coal formation and its structure. Techniques, such as solid NMR, pyrolysis, and fast bombardment mass spectrometry, are used to study the macromolecules in coal macerals. The physical structure of coal and structure stability are investigated by inverse chromatography and NMR. Information obtained in this study should ultimately help develop more efficient and cleaner ways to use coal. [7.0 FTE]

## Brookhaven National Laboratory
## Upton, Long Island, New York 11973

### Department of Applied Science $672,000

### 94. *High-Temperature Chemistry*

*J.J. Egan*

This study of the thermodynamic and transport properties of inorganic substances at high temperatures attempts to explain the results in terms of appropriate atomic models. Substances include solid and liquid compound semiconductors, solid electrolytes, and molten salts. Electrochemical techniques are used to investigate the effect of composition on the concentration, mobility, and diffusion of electrons and electron holes in these substances. Cells employing solid electrolytes at high temperatures as well as molten salt electrolytes prove especially useful for characterizing these systems. High-temperature calorimetry is being used to study liquid semiconductors and other liquid alloy systems. Molten salts are studied since they are important for the development of high energy-density batteries and fuel cells. The electronic conductivity of these melts in particular is examined by special techniques. Solid compound semiconductors of potential use as solar cells are studied by high-temperature electrochemical techniques. [2.9 FTE]

### 95. *Metal Hydrides*

*J.J. Reilly*

This project focuses on determining the thermodynamic properties and structural parameters of metal alloy–hydrogen systems. Specific goals are (1) to relate hydriding properties of metal alloys to their structure and composition, (2) to determine alloy–hydrogen phase diagrams, (3) to determine and systematize crystal structure, and (4) to relate all pertinent data and observations to predict the behavior of a given alloy–hydrogen system. Current topics of interest are the causes of the observed deviations from ideal behavior of certain intermetallic hydrogen systems, surface and near-surface properties of metal–hydrogen systems, structure of metal hydride phases, crystal structure refinement methods for highly strained metals, and reaction kinetics of metal hydride suspensions. Major experimental tools and/or techniques are x-ray and neutron diffraction, equilibrium pressure temperature composition measurements, ion beam analysis, and magnetic susceptibility measurements. [4.5 FTE]

### Chemistry Department $300,000

### 96. *Organometallics in Homogeneous Catalysis*

*R.M. Bullock*

This project clarifies the role that soluble transition metal complexes can have in the homogeneous catalytic activation of organic or small molecule substrates. Potential long-term goals include the discovery of more efficient catalysts and the development of new insights into the mechanisms of both homogeneously and heterogeneously catalyzed processes. A specific example is the transition metal-catalyzed reaction of olefins with $H_2$ and CO to form aldehydes (the hydroformylation reaction). Evidence for the importance of radical pathways in this reaction will be sought by studying the reactions of a series of metal hydrides of the type $HM(CO)_n$ with suitably chosen olefins. Another example is the reaction of metal hydrides with metal alkynyl complexes to form dimetalla alkenes or bridging vinylidene complexes. A series of metal hydrides of known acidity will be investigated to test the relative importance of proton and hydride transfer reactions in this system. [2.2 FTE]

### 97. *Mechanisms of Photo-, Enzyme-, and Chemically Catalyzed* Cis-Trans *Isomerization*

*S. Seltzer*

*Cis-trans* isomerization can be brought about by the application of heat or light, or by catalysts. Because the physical and chemical properties of the two isomers differ, relaxation of a nonequilibrium mixture of isomers (achieved by irradiation) to the equilibrium mixture can result in the release of thermal or electrical energy. This *cis-trans* energy-producing effect is used in biological processes such as vision in animals and the light-driven proton pump of halobacteria, which can be used in a photogalvanic cell. Studies at Brookhaven National Laboratory are concerned with mechanisms of *cis-trans* isomerization catalyzed by chemical reagents, by enzymes, and by light, and their applications to the mechanism of the bacteriorhodopsin proton pump. [1.4 FTE]

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

### Materials and Molecular Research Division — $982,000

### 98. *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 (e.g., $C_xF_{1-\delta}\cdot\delta HF$) may find use in high-energy electrodes. Physical 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]

### 99. *Catalytic Hydrogenation of Carbon Monoxide*
*A.T. Bell, G.A. Somorjai*

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, 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 invovled in carbon monoxide hydrogenation. [8.0 FTE]

### 100. *Transition Metal Catalyzed Conversion of CO, NO, $H_2$, and Organic Molecules to Fuels and Petrochemicals*
*R.G. Bergman*

The central objective of this project is the discovery of new chemical reactions between organic compounds and transition metals, and the understanding of how these reactions work. In 1982, a major discovery of this project was the finding that certain iridium complexes undergo oxidative addition into the carbon–hydrogen bonds of completely saturated hydrocarbons (alkanes). This was the first example of this long-sought C–H activation reaction. Research carried out since this discovery has been aimed at (1) understanding the fundamental physical principles that control this type of reaction, and (2) exploring methods for utilizing the C–H activation reaction to develop processes for converting alkanes into functionalized organic molecules. Recent studies have made significant progress on understanding the mechanism of iridium C–H activation reactions, and uncovered two other transition metals (rhodium and rhenium) that, when properly substituted, also insert into alkane C–H bonds. [4.0 FTE]

### 101. *Formation of Oxyacids of Sulfur from $SO_2$*
*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. Recent research has elucidated the kinetics of the exchange of oxygen atoms between bisulfite ion and water, using the nuclear magnetic resonance of $^{17}O$ for following the reaction. In work supported by EPRI, the kinetics of the oxidation of bisulfite ion by oxygen has been studied. Work remains to be done on the latter project and additional oxidation-reduction reactions of bisulfite should be investigated. Of particular interest are such reactions involving two or more oxidation states of sulfur itself, e.g., reactions involving $HSO_3^-$, $H_2S$, $S_8$, 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 of such systems is underway and some results for a two-dimensional model have been published. The work will be extended to three dimensions using a more sophisticated model for water. [1.5 FTE]

### 102. *Synthetic and Physical Chemistry*
*W.L. Jolly*

The objective of the photoelectron spectroscopic part of this project (which is concluding) is 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]

### *103. Surface Chemistry: Application of Coordination Principles*
*N.E. Phillips*

The research objective is to define the coordination chemistry of transition metal surfaces on a comparative basis with that of molecular metal complexes and molecular metal clusters. Displacement reactions supplemented with diffraction and spectroscopic data will be used to elucidate structural, bonding, and chemical features of silicide, nickel, and platinum metal surfaces with chemisorbed molecules. Studies focus on the chemisorption states of aromatic hydrocarbons, olefins, amines, nitriles, and acetylenes on these surfaces. Theoretical analysis, based on symmetry matching of energetically available metal surface orbitals with those of molecules and molecular fragments of hydrocarbon, has been developed for a further comparison with structural data. [1.8 FTE]

### *104. Potentially Catalytic and Conducting Oligoorganometallics*
*K.P.C. Vollhardt*

The project objective is to design and synthesize novel organometallic compounds that exhibit new properties as potential catalysts in reactions to be used in the conversion of coal to liquid and gaseous fuels. In addition, the aim is to specifically construct new molecules that may activate organic chemicals to new reactions and that by virtue of their unusual topology and/or electronic make-up may be important new materials, such as photostorage devices, photocatalysts, and conductors. Recent work has centered on the novel and unusual chemistry of fulvalene dimetals, which has led to the discovery of unprecedented binuclear chemistry of homo- and heteronuclear transition metal derivatives. Several of these compounds have shown novel and distinct chemistry relevant to catalysis, surface reactions, and photochemical storage cycles. Work on fulvalene dichromium, molybdenum, tungsten, and ruthenium and their mixed heterodinuclear analogs has uncovered (1) new binuclear modes of hydrogen evolution from dihydrides, (2) chemo- and region-specific catalytic hydrogenation of 1,3-dienes and carbon monoxide, (3) carbon–carbon bond formation through biscarbenes, (4) the occurrence of unprecedented mechanisms of photosubstitution, and (5) the utilization of photochemically activated complexes in thermal processes. [3.0 FTE]

# Los Alamos National Laboratory
# Los Alamos, New Mexico 87545

## Isotope and Nuclear Chemistry Division $238,000

### *105. Transition Metal Mediated Reactions of $SO_2$*
*G.J. Kubas, R.R. Ryan*

The objective of this project is to delineate the basic chemistry of $SO_2$ reactions mediated by transition metal complexes, particularly the mechanistic aspects of catalytic or potentially catalytic conversions of $SO_2$ to harmless products such as sulfur. Homogeneous catalytic reduction of $SO_2$ by hydrogen using catalysts such as metal sulfide complexes is being studied to determine reaction rates, mechanisms, and catalyst stability to oxidation or sulfidation. Metal sulfide catalysts have been chosen (1) to circumvent the latter problem and (2) because of their use in hydrodesulfurization processes. Heterogeneous catalytic conversions of $SO_2$ will be carried out in order to determine potential applications for $SO_2$ emission control. Homogeneous reduction of nitrogen oxides both in the presence and absence of $SO_2$ is also being studied since most waste gas streams contain $NO_x$, which, like $SO_2$, also contributes to acid rain. Another facet of our work involves oxygen transfer reactions of $SO_2$ that are of potential relevance to atmospheric oxidation of $SO_2$ to $SO_3$. We have recently observed that certain metal complexes promote $SO_2$ disproportionation to $SO_3$-containing moeities and will explore the mechanisms of these processes further. As a spinoff of the studies of $SO_2$ bond activation, activation of the H–H bond in hydrogen is also being investigated in complexes that contain the first examples of molecular hydrogen coordination. [1.6 FTE]

# Oak Ridge National Laboratory
# Oak Ridge, Tennessee 37831

## Chemical Technology Division $362,000

### *106. Kinetics of Enzyme-Catalyzed Processes*
*E. Greenbaum, J. Woodward*

This project focuses on the physicochemical mechanisms of artificial photosynthetic systems including: (1) the reconstituted *in vitro* system composed of isolated spinach chloroplasts, ferredoxin, and hydrogenase (CFH) and (2) the substituted systems in which nonbiological catalysts are electronically linked to water splitting and chloroplast-reducing power. Research on the fundamentals of stabilization and immobilization of cellulase is also performed. Colloidal platinum has been prepared and precipitated directly onto chloroplast photosynthetic membranes. This system is capable of the simultaneous photoevolution of hydrogen and oxygen. Experimental data support the interpretation that part of the platinum metal catalyst is precipitated adjacent to the photosystem I reduction site of photosynthesis and that electron transfer occurs across the interface between photosystem I and the catalyst. Photoactivity of this material is dependent on the nature of the ionic species from which the platinum is precipitated. All photoactive samples were prepared from the hexachloroplatinate(IV), $[Pt(Cl_6)]^{2-}$, ion, whereas samples prepared by precipitation of the tetraamineplatinum(II), $[Pt(NH_3)_4]^{2+}$, ion showed no hydrogen evolution activity and only transient oxygen activity. An inorganic-based support for cellulase has been developed. The functional group on the support to which cellulase adsorbs is concanavalin A. This material has the potential to adsorb (and recover) cellulase from solution. [3.3 FTE]

## Chemistry Division $2,231,000

### *107. Organic Chemistry and the Chemistry of Fossil Fuels*
*A.C. Buchanan, B.M. Benjamin, L.L. Brown, E.W. Hagaman, R.R. Chambers, F.M. Schell*

The goal of this fundamental research project on the organic chemistry of coal is an improved understanding of the structure and reactivity of this complex substance. These studies will contribute to the scientific base necessary for the development of novel processes for the use of coal as a source of fuels and chemicals. The current project has three principal interrelated tasks. Solid-state $^{13}C$-NMR methods including double cross polarization techniques are developed for the study of coal structure, particularly in combination with chemical modifications that selectively introduce NMR active nuclei (e.g., $^{31}P$, $^{13}C$) as probes. Secondly, chemical reactions are designed to quantitatively diagnose significant structural features in coal. Acid-catalyzed transalkylation is used to probe aliphatic structures, while strong base chemistry is used to categorize acidic C–H and O–H sites in coal. These studies are substantially enhanced by parallel studies with model compounds. Finally, the thermal reactivity of coal is modeled with emphasis on unraveling the effects of surface immobilization on the thermolysis of $\alpha,\omega$-diphenylalkanes covalently bound to a silica surface. [7.7 FTE]

### *108. Basic Aqueous Chemistry to High Temperatures and Pressures*

*R.E. Mesmer, H.F. Holmes, W.L. Marshall, D.A. Palmer, J.M. Simonson*

The project objective is to study the chemical and thermodynamic properties of broad classes of solutes in water at high temperatures and pressures to establish bases for predictability and fundamental understanding of their chemical reactivity. The essence of the chemistry that has been studied is (1) the thermodynamic properties of single and mixed electrolytes and nonelectrolytes (including water itself); and (2) the dynamics and equilibria involved in the interactions between electrolytes (e.g., ion association, neutralization, complexation, and oxidation-reduction reactions), between dissolved solutes and water (hydrolysis reactions), and between solid or gas phases and water (solubility and phase-change processes). Progress is dependent on the parallel development and adaption of a range of diverse, but complementary, experimental techniques to provide precise data at high temperatures, and in some instances, supercritical conditions. These are principally calorimetry, conductivity, potentiometry, spectrophotometry, density, isopiestic, and phase-study measurements. New efforts focus on obtaining volumetric and Raman spectroscopic information using new cells developed in the project. Results have direct application to steam generation, fuel reprocessing, metal refining, the disposal of wastes, and the extraction of heat and materials from natural resources. [4.9 FTE]

### *109. Heterogeneous Catalysis Related to Energy Systems*

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

This project involves two related activities. In the first, the technique of low-energy alkali ion scattering as a surface-specific structural tool is being developed and applied to the study of clean and adsorbate-covered surfaces of catalytic interest. Comparison of the experimentally observed energy and angle dependencies of the scattered ions with computer simulations allows for quantitative descriptions of surface structure. These methods have been applied to study surface reconstruction of gold(110); bonding geometry and ordering of oxygen, carbon, nitrogen, and sulfur overlayers on molybdenum(001) and molybdenum(111); surface structure of amorphous $Fe_{80}B_{20}$ ribbon; and surface layer relaxations on molybdenum(111). The newer second activity will examine surface adsorption on metal sulfide surfaces in ultrahigh vacuum by electron energy loss spectroscopy and by thermal desorption spectroscopy. A sample transfer system will permit the sample to be moved to an adjoining high-pressure cell that will be used for monitoring hydrodesulfurization reactions over a wide pressure range. Measured reactivity and selectivity will be correlated with changes in the surface modified by introducing structural defects, bulk or surface impurities, or changes in stoichiometry. [2.2 FTE]

### *110. Molten Salt Catalysts for Clean Fuel Synthesis*

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

This research is a basic investigation of molten salts as catalytic reaction media and as media for the characterization of reactive organic intermediates. Selected aspects of Friedel-Crafts catalysis are currently under study with the aid of highly purified ionic liquids that have high $AlCl_3$ activities, such as the compound 1-ethyl-3-methyl-1H-imidazolium heptachlorodialuminate, $EMI(Al_2Cl_7)$. This compound remains liquid at very low temperatures and has an $AlCl_3$ activity close to unity (the highest value possible). We are investigating the intrinsic behavior of arenes and heterocyclic aromatic compounds, and reactive intermediates formed from them in these high $AlCl_3$-activity liquids with the aid of a battery of *in situ* instrumental techniques including ESR, NMR, optical spectroscopy, and electroanalytical and spectroelectrochemical procedures. [3.2 FTE]

## Pacific Northwest Laboratory
## Richland, Washington 99352

| **Chemical Technology Department** | **$508,000** |
|---|---|

### *111. Hydrogenation Mechanisms of Coal*

*J.A. Franz, M.S. Alnajjar, D.M. Camaioni*

This project focuses on determining the energetics and mechanisms of free-radical reactions related to thermal dissolution of coal in hydrogen donor media. Relative rates of radical rearrangements, atom transfer reactions, fragmentation reactions, and charge transfer reactions are being determined; absolute rates are determined by kinetic laser flash spectroscopy for key atom transfer reactions. The cyclization of o-allylbenzyl radical to 2-indanylmethyl radical, for example, is used as an intramolecular free-radical clock to compare atom transfer rates to benzylic radicals, thereby determining the relative donor strength of a wide variety of coal-related donors. Carbon–sulfur bond-making and -breaking reactions and sulfur-centered radical intermediates are being studied. [2.0 FTE]

### *112. Thermochemical Liquefaction of Lignocellulosic Materials*

*D.A. Nelson, R.T. Hallen*

The purpose of this research is to determine the reaction mechanisms involved in the hydrothermolysis (aqueous liquefaction) of lignocellulosic materials. Liquid products from cellulose, lignin, hemicellulose, and protein or respective chemical models are investigated over a range of conditions, including temperatures up to 350°C. Amino acids or amines act as catalytic agents to enhance specific product formation during hydrothermolysis. Reaction products are very dependent upon pH; the major products are furans under acidic conditions and aromatics under basic conditions. Elucidation of the reaction mechanisms is studied with isotopically labeled compounds. Synthesis of various models for lignin revealed that the presence of an oxygen atom at the ortho position of phenoxy rings had a much greater influence on stereochemical control during reduction than had been recognized. [0.9 FTE]

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

**Surface Science Division** **$354,000**

### *113. Surface Catalytic Studies*
*D.W. Goodman*

The goal of this research is to develop an understanding of surface catalyzed reactions at the molecular level using the full complement of modern surface analytical techniques. Of primary importance are those reactions relating to the synthesis of hydrocarbons from $H_2$ and CO. The experimental work includes the determination of reaction kinetics of hydrocarbon formation and rearrangement over single crystal catalysts. The work is carried out in a custom-built ultrahigh vacuum apparatus allowing both kinetic measurements and surface analysis. Recent studies have addressed the mechanism by which poisons and promoters alter catalytic activity and selectivity as well as the metal site requirements for catalytic activity. These measurements have utilized careful dosing of impurity atoms, either electronegative (e.g., sulfur), neutral (e.g., silver, copper), or electropositive (e.g., potassium), onto a catalytically active single crystal substrate (e.g., nickel, ruthenium, rhodium). These studies have established a relationship between the electronic nature of the impurity atom and its ability to alter the catalytic activity of the substrate for certain reactions. Recent work has shown that unique catalytic behavior can be obtained by combining elements on a solid surface. For example, submonolayer amounts of copper on the Ru(0001) surface yield catalytic properties that are not like those of copper or ruthenium but exhibit greatly improved behavior for certain reactions. These strained crystalline overlayers represent a promising new field of strained layer catalysts. [2.5 FTE]

## Solar Energy Research Institute
### Golden, Colorado 80401

**Solar Fuels Research Division** **$206,000**

### *114. Mediated Electrochemical Reduction of $CO_2$*
*D.L. DuBois*

This research involves the synthesis and characterization of metal phosphine complexes for evaluation as catalysts for the electrochemical reduction of $CO_2$, and includes structural, spectroscopic, and electrochemical studies of the metal complexes. The project objective is to elucidate factors important in promoting (1) reversible two-electron redox processes and (2) electrochemical reduction of $CO_2$. A number of complexes of the type $[Pd(triphos)(PR_3)](BF_4)_2$ have been prepared and found to be catalysts for the electrochemical reduction of $CO_2$ to CO. Mechanistic studies of these catalysts are in progress. Incorporation of these complexes into polymers is studied to develop electrocatalytic modified electrodes. A number of analytical techniques are used to characterize these polymers in oxidized and reduced forms. These techniques include cyclic voltammetry, infrared spectroscopy, UV-VIS spectroscopy, and $^{31}P$ NMR spectroscopy. *In situ* spectroelectrochemical studies of the modified electrodes are possible in favorable cases. [0.2 FTE]

### *115. Basic Research in Synthesis and Catalysis*
*J.C. Smart, C.J. Curtis*

This project involves the synthesis, characterization, and reaction studies of transition metal coordination complexes and organometallic compounds for the photoconversion of CO, $CO_2$, and related substrates to fuels and chemicals. It includes structural, spectroscopic, and mechanistic studies for understanding the interrelationship of molecular geometry, electronic structure, and catalytic activity. Designed organometallic synthesis has yielded new bi- and trimetallic complexes with bridging fulvalene, *s*- and *as*-indacene, and trindene ligands of titanium, zirconium, tantalum, molybdenum, manganese, and cobalt. Reactions of CO with early transition metal hydride complexes are studied to develop $H_2/CO$ catalysts. For example, the reaction of a zirconium hydride complex containing a bridging fulvalene ligand with CO results in a bimetallic zirconium complex containing a bridging formaldehyde ligand. Fulvalene-bridged tantalum complexes containing alkylidene ligands have also been prepared. Spectroscopic and photochemical studies of cobalt and nickel metallofulvalene and metalloindacene are contributing to an understanding of their electronic structures and the potential utility of their low-lying excited states in photocatalysis. [1.25 FTE]

# Separations and Analysis

## Ames Laboratory
## Iowa State University
### Ames, Iowa 50011

**Processes and Techniques Program** **$968,000**

### *116. Analytical Spectroscopy*
*V.A. Fassel*

This project entails systematic observation of spectroscopic phenomena in order to derive new spectroscopic analytical concepts that offer promise of solving singularly difficult analytical problems in the various fields of energy generation (e.g., conversion of coal to liquid and gaseous fuels, recovery of shale oil, solid-state materials research, and environmental pollution assessment). Emphasis is on: (1) novel applications of electrical plasmas as vaporization-atomization-excitation-ionization sources for analytical atomic emission, mass, and fluorescence spectroscopy; (2) analytical applications of highly selective energy transfer from energetic, long-lived species to trace level organic or inorganic constituents leading to optical emission; (3) use of processes developed in (2) to devise noble-gas afterglow, GC or LC detectors for element-specific, multielement speciation at trace concentration levels; and (4) photoacoustic and thermal wave-imaging processes and their analytical applications. [3.6 FTE]

### *117. Analytical Separations and Chemical Analysis*
*J.S. Fritz*

A major effort is underway to improve methods of ion chromatography and liquid chromatography of metal chelates, so that complex mixtures of inorganic anions and cations can be separated and analyzed with the same facility that is possible in organic chromatography. Research on ion-exchange resins is designed to provide better resins for chromatography and to give a better understanding of the important scientific problem of resin selectivity. New methods are being developed for the selective concentration of various organic compounds prior to chromatographic analysis. Improved statistical theories of chromatography are being formulated to correct some inadequacies of prevailing theories and provide a better foundation for chromatography. [2.8 FTE]

### *118. Mass Spectroscopy in Chemical Analysis*
*R.S. Houk*

The general objective of this project is to develop, evaluate, and characterize ionization techniques with potential value for analytical mass spectrometry (MS). Current efforts concentrate on improving techniques for extracting and mass-analyzing ions from inductively coupled plasmas (ICPs). The value of this ion source for elemental and isotopic analysis of solutions on a rapid, direct basis is being demonstrated. Various alternate techniques for introducing samples are being studied with the ICP-MS device as an element-selective, isotopically sensitive detector. These sample introduction methods include electrothermal furnaces or arc discharges for direct vaporization of solids and liquid chromatographic separations for determining elemental speciation via isotopic tracing experiments. Mass spectra of polar, nonvolatile organic compounds can be obtained directly from aqueous solutions, provided ICP conditions are properly cooled. Temperatures, ion and electron densities, and energy transfer processes in ICP are being modeled and studied experimentally. Ionization techniques for mass spectrometric analysis of solids are also investigated. These techniques include a laser probe for direct, absolute elemental analysis and a pulsed neutral atom beam for desorption and ionization of nonvolatile organic molecules. [2.8 FTE]

### *119. Lasers in Analytical Chemistry*
*E.S. Yeung*

This project will develop new analytical techniques relevant to pollution monitoring, combustion diagnosis, and material evaluation in energy production. New spectroscopic concepts and instrumentation (particularly those involving lasers) are studied so that analytical methods can gain in sensitivity, selectivity, accuracy, and speed. Focus is on: (1) the development of the laser microprobe for atomic spectroscopy on surfaces; (2) new optical detectors for liquid chromatography suitable for complex organic samples; (3) nonlinear Raman methods and two-photon methods applied to analytical problems; (4) photoacoustic and interferometric concepts for improved absorption measurements, especially in flow systems; (5) high-resolution spectroscopy for stable isotope ratio determinations; and (6) laser-induced chemiluminescence for specific gas analysis. Investigations include the fundamental principles behind the measurements, evaluation of the analytical potentials, and demonstration of the analytical method in representative samples. [6.1 FTE]

## Argonne National Laboratory
## Argonne, Illinois 60439

**Chemistry Division** **$1,072,000**

### *120. Separations Science Related to Nuclear and Hydrometallurgical Technology*
*E.P. Horwitz*

The project objectives are (1) discovery of new separation processes and energy-efficient techniques applicable to nuclear and hydrometallurgical technologies and (2) elucidation of the basic chemistry involved. Major areas of investigation are: (1) basic studies of transuranic extraction chemistry with bifunctional extractants; (2) elucidation of the structures of extractants and metal ion–extractant complexes in nonaqueous media; (3) synthesis and characterization of new extractants for metal ion separation by solvent extraction; and (4) evaluation of the separation potential of new extractant systems, with emphasis on new methods for by-product recovery from radioactive waste, energy-efficient techniques for the recovery of critical and strategic materials from low-grade domestic sources, and new methods for processing radioactive waste streams. [10.5 FTE]

### *121. Particle-Induced Desorption/Ionization Mass Spectrometry*
*J.E. Hunt*

The general phenomena whereby gas-phase ions are produced by bombardment of organic compounds in the condensed phase with high-energy ions or atoms is called particle-induced desorption/ionization. Detection of such ions by mass spectrometry has revealed amazingly large, intact ions (i.e., proteins, nucleic acids, enzymes). The project objective is to provide an understanding of phenomena that occur as a result of particle impact, to improve the analytical utility of particle-induced desorption mass spectrometric techniques. Results of this study bear on the analytical usefulness of several mass spectrometric methods that depend on particle impact for ion production. Other results also provide important quantitative knowledge of the limiting features of ion yield and sensitivity for these mass spectrometric methods. [1.1 FTE]

## Brookhaven National Laboratory
## Upton, Long Island, New York 11973

**Department of Applied Science** **$495,000**

### *122. Specific Molecular Property Detectors for Chromatographic Analysis*
*J.S. Gaffney, E.T. Premuzic*

We are studying novel specific molecular property detectors for use in gas and liquid chromatography. Detection schemes are devised that simplify the separation analyses by increasing the detector response for the specific molecules of interest while reducing the background noise from potential interferences. Areas of application range from process monitoring to trace analysis in organic geochemistry, environmental, and biomedical investigations. The project is currently developing monitoring devices for specific hydrocarbons and hydrocarbon classes. Use of vacuum ultraviolet (130 to 300 nm) circular dichroism (CD) is under investigation as a means of monitoring optically active hydrocarbons eluting from a gas chromatograph (GC). This GC/CD system is using the National Synchrotron

Light Source U9A Beamline. The spectral and thermal properties of ozone-chemiluminescence as a means of monitoring hydrocarbon classes (e.g., reduced sulfur compounds, olefins, and so forth) and photothermal laser spectroscopies are also being investigated as selective and sensitive devices for chromatographic detection. [1.8 FTE]

### 123. *Analytical Techniques with Synchrotron Radiation and Ion Beams*
*K.W. Jones, B.M. Gordon*

This project develops new analytical techniques for elemental determinations and chemical speciation using synchrotron radiation from the National Synchrotron Light Source (NSLS). Equipment is being designed to produce a focused monoenergetic x-ray beam with a spatial resolution in the neighborhood of 10 micrometers. Other apparatus has been assembled that uses a collimator with either monoenergetic x rays or white radiation to produce beams with sizes around 30 micrometers. The x rays from the NSLS have energies between about 4 and 20 keV, which will make possible investigation of all elements in the periodic table with $Z > 10$. Techniques for precise trace element measurements with minimum detectable limits approaching one part in $10^9$ are being developed concurrently for both bulk and microanalysis. Chemical speciation will be achieved by use of precision x-ray energy measurements and electron spectroscopy techniques. A searching test of the new methods is made by comparison of the results obtained with synchrotron radiation with those obtained by other methods. These tests require the application of the techniques to samples obtained from a variety of energy-related fields. The use of synchrotron radiation for elemental quantification is supported by the use of nuclear ion-beam analysis, which makes available complementary analytical techniques that are used to corroborate and extend the synchrotron radiation results. [4.4 FTE]

## Idaho National Engineering Laboratory
## Idaho Falls, Idaho 83415

**EG and G Idaho, Inc.** **$135,000**

### 124. *Negative Ionization Mass Spectrometry*
*J.E. Delmore*

This program studies two ionization processes for application to negative ion mass spectrometry: negative surface ionization and electron capture. Surface ionization studies focus on systems where the species of interest are chemisorbed on a low work function surface, followed by thermal desorption. Ionization efficiency has been increased by several orders of magnitude using this technique. This technology is currently used for the *in situ* study of catalysis mechanisms. A unique electron capture ion source using crossed electric/magnetic fields has been theoretically modeled, designed, constructed, and tested. This ion source forces electrons into cycloidal orbits, reducing their kinetic energy to thermal values, thus enhancing their capture by certain gas molecules to form negative ions. Some of these negative ion species spontaneously detach an electron after a few to tens of microseconds, and the properties of these types of negative ions are being studied to develop high-energy neutral particle beams. [1.0 FTE]

## Monsanto Research Corporation–Mound
## Miamisburg, Ohio 45342

**Nuclear Operations Department** **$471,000**

### 125. *Isotope Separation Research and Development*
*W.M. Rutherford, B.E. Jepson, E.D. Michaels, W.R. Wilkes*

This project will investigate chemical exchange and liquid-phase thermal diffusion as techniques for stable isotope separation. The chemical exchange work is directed toward finding significant equilibrium isotope effects in metal isotope exchange reactions emphasizing macrocyclic complexants to develop two-phase isotope exchange processes for practical separations. The liquid thermal diffusion work is directed toward (1) further development of the recently discovered 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. [3.6 FTE]

### 126. *Atomic and Molecular Properties and Their Relationships to Separation Processes*
*W.L. Taylor, G.T. McConville*

The objective of this research is to investigate physical properties of isotopes and their mixtures pertinent to the development or improvement of new or existing technologies. Experimental and theoretical work on gas transport properties and thermodynamic properties of gases, liquids, and solids is conducted and applied to improving methods of isotope separation and the use of isotopes and their mixtures. Thermal and ordinary diffusion coefficients are measured and separation processes studied in the context of nonequilibrium thermodynamics. This project also investigates several properties of the hydrogen isotopes and their spin isomers. Experiments are carried out to determine the isotopic exchange rate between deuterium and tritium at low temperatures and to characterize the effect of trace impurities and surface conditions on the exchange rate. A system is being prepared to separate the nuclear spin isomers of deuterium. Specially constructed cells loaded with ultrahigh-purity deuterium produced at Mound are evaluated as part of an international effort to get the triple point of $D_2$ established as a fixed point in the International Temperature Scale. Theoretical studies on the hydrogen molecule interaction have produced the best available spherically symmetric intermolecular potential for the hydrogen isotopes. Current work is aimed at incorporating the angle dependence into the collision dynamics. [3.3 FTE]

## Oak Ridge National Laboratory
## Oak Ridge, Tennessee 37831

**Analytical Chemistry Division** **$1,454,000**

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

This program involves the study of secondary ionization of organic compounds and resonant photoionization of sputtered atoms and small molecules. Physical and chemical interactions of various organic compounds dissolved in different matrices are related to the secondary ion mass spectrometry (SIMS) of such solutions. The focus is on finding matrices that enhance secondary ion emission for particular compound classes. A singular result of these studies is our finding that sulfuric acid solutions of polar-substituted polynuclear aromatic compunds (PACs) yield copious secondary ions characteristic of the dissolved PAC. These compounds are generally involatile, mutagenic, teratogenic, and carcinogenic, and their detection and identification is difficult when other techniques are used. In contrast, work with inorganic samples emphasizes generating ions whose intensity is independent of the sample matrix. The hallmark of resonance photoionization of sputtered neutral atoms is that the matrix from which the atoms were sputtered does not affect the ionization. The well-known selectivity characteristic of resonance ionization is explotied by using a Nd:YAG pumped dye laser to ionize atoms such as uranium and samarium sputtered from particulate samples. [2.0 FTE]

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

This project centers on ionization/excitation methods and instrumental techniques in organic mass spectrometry. Specifically, the instrumental focus is on the chemical and physical principles underlying mass spectrometry/mass spectrometry (MS/MS). Ionization/excitation methods are studied to enhance the sensitivity and specificity of MS/MS and to increase the information obtainable. The physical and chemical phenomena that take place in the MS/MS instrument are investigated, using primarily MS/MS, to gain a better understanding of the wide variety of possible reactions. The analytical utility of many of these reactions is a new area of investigation. Results can point to possible instrumental modifications to improve the MS/MS experiment, and can also lead to improvements in single-stage organic mass spectrometry. The studies on ionization methods have potential applicability not only to single-stage mass spectrometry but also to other analytical techniques that rely on the ionization of organic molecules. [2.6 FTE]

### *129. Advanced Spectroscopic Methods for Chemical Analysis*
*L.D. Hulett, J.M. Dale, D.L. Donohue,
T.M. Rosseel*

This project applies electron, positron, x-ray, and heavy-ion physics to analytical problems. Special emphasis is on materials characterization. Positron spectroscopy is being used (1) to determine surface areas of solid powders and (2) to study surfaces and defect structures of carbon fibers used in composite materials. A scheme for nondestructive analysis of epoxy–carbon fiber composites is being studied. The technique for generating monoenergetic positrons, developed earlier in this project, is being used in the construction of an intense monoenergetic positron beam facility, in which the Oak Ridge Electron Linear Accelerator (ORELA) will be used as a source of positrons. Fast heavy ions extracted from the EN Tandem Accelerator and the Holifield Heavy Ion Facility are being used to excite x-ray fluorescence from solids. Heavy ion-induced x-ray satellite emission (HIXSE) spectra contain information relating to valence states of metal alloys and other materials. The positron and heavy-ion methods involve close interactions with other DOE projects such as the High Temperature Materials Laboratory (HTML). The University of Tennessee Engineering Department is contributing material and certain personnel specialties to this work; other institutions involved are the State University of New York, Fredonia, and several universities in the eastern and southern United States. [2.8 FTE]

### *130. Research Development and Demonstration of Advanced Chemical Measurement Techniques*
*J.M. Ramsey, H.H. Ross, R.W. Shaw,
W.B. Whitten, J.P. Young*

The objective of this work is to provide advanced measurement techniques for chemical analysis. New concepts and technologies are explored in relation to their analytical potential. We are continuing to investigate the use of phase conjugate optical techniques to control the bandwidth and wavelength tuning of dye lasers. Degenerate four wave mixing, a way to perform optical phase conjugation, is evaluated as a possible analytical spectroscopy tool. Alternative atomization techniques are considered that allow the full advantages of this Doppler-free spectroscopy to be realized. This effort is an attempt to develop a viable approach to optical isotope analysis. Molecular spectroscopy in seeded supersonic beams is studied. This technique also allows Doppler-free spectroscopic measurements, and is applied to internal combustion engine diagnostics and microwave spectroscopy. Work is continuing on the fluorescence spectrocopy studies of transuranium elements in host matrices. The goal is to find sensitive methods for detection of the actinide elements. Efforts to obtain diagnostic tools for chemical vapor deposition processes will be maintained. We will initiate a project in new concepts in radionuclide detection and measurement. These methods will combine conventional approaches with new advanced technologies such as optical waveguides, bioconcentration, and the use of machine intelligence. [3.5 FTE]

### *131. Mass Spectrometric R&D for Inorganic Analyses*
*R.L. Walker, H.S. McKown, R.W. Shaw,
D.H. Smith, J.P. Young*

The program goal is to improve isotopic ratio mass spectrometry and to expand its areas of application. Improvements in instrumentation and methodology are sought that lead to better precision and sensitivity and enhanced specificity. Isotope dilution is extensively used to provide quantitative results. A class 100 clean room is used for preparation of small samples and development of low-level separations techniques. One area of emphasis is resonance ionization mass spectrometry (RIMS). The processes leading to ionization for three lanthanide elements have been explored using our electron spectrometer. A copper-vapor laser is being evaluated for application to isotope ratio measurements of uranium and neodymium. Another significant area is to develop new methodology for isotopic analysis of a wide variety of elements. We have to date developed techniques for mercury, tellurium, and beryllium. The application of internal standards to problems encountered in the nuclear fuel cycle continues to be emphasized. [2.4 FTE]

## **Chemical Technology Division $1,262,000**

### *132. Chemical and Physical Principles in Multiphase Separations*
*C.H. Byers, R.M. Wham, J.S. Watson,
T.C. Scott*

This program is comprised of several fundamental studies that address the issue of efficiency of energy utilization in separation processes. Focus is on improving mass transfer in liquid–liquid solvent extraction and on the use of external fields to improve fluid–fluid and solid–fluid separation systems. Enhancement of mass transfer rates in extraction is produced through the use of pulsing electric fields. Investigations in this area include mechanics of droplet oscillation, hydrodynamics of the droplet–contiuum system, and mass transfer studies. Imposing an electric field upon droplet formation devices allows for increased control of the size of droplets formed. Theoretical analysis is under way to determine the energy input by the field and to predict droplet sizes. AC and DC fields are also used to study stabilized expanded beds of solids. Studies have been undertaken on liquid–solid and gas–solid systems that yield well-characterized, uniform-bed expansion. These studies are directed towards better understanding of hydrodynamic and mass transfer phenomena that occur in expanded particle systems. [4.0 FTE]

### *133. Solvent–Solute Interactions in Separations with Supercritical Solvents*

*H.D. Cochran, J.S. Watson*

This project is a fundamental experimental and theoretical study of the molecular interactions between supercritical solvents and dissolved inorganic solutes. Solubility in simple, nonpolar solvents is studied initially, but polar, H-bonding, and complex-forming solvents will be studied in the future. Recent progress in the theoretical studies in this project allows treatment of these more difficult systems in a fundamental way that has not been possible before. Current experimental studies focus on measuring solubility of transition metal fluorides in supercritical substituted-methane solvents. These experiments provide data to test our theoretical model for systems substantially different from those studied by other researchers. Independent experimental measures of the solvent–solute interactions by NMR relaxation studies of supercritical solutions are planned for the future. Fundamental data and theories of the molecular interactions in supercritical solutions of inorganic solutes will considerably broaden the available data base, provide models for multicomponent phase equilibrium calculations for separations processes, and potentially aid in developing generalized models that are applicable to inorganic compounds. [1.8 FTE]

### *134. The Dynamics of Sorption and Its Role in Chemical Separations*

*P.W. Fisher, J.S. Watson*

The purpose of this project is to develop a fundamental understanding of sorption, and especially the dynamics of sorption, as it relates to separations. Many chemical separations utilize sorption as the primary separation phenomenon, or as an important step in the overall separation mechanism. Whenever a mixture is brought into contact with a surface to effect a separation, the first step at the surface is always absorption, and the last step is always desorption, regardless of the intervening steps. Emphasis in this project is on the dynamics of this process. The goal of the work is to obtain theoretical relationships between the intermolecular forces that control these processes, and the dynamic and static effects that can be measured experimentally. The work will be applicable to separations of both multicomponent gaseous and liquid mixtures. [1.4 FTE]

### *135. Chemistry of Actinides and Fission Products*

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

This program aims to develop the fundamental chemistry of the actinide elements and their fission products. Specific areas of focus include: (1) photochemical studies of the aqueous actinides and fission products; (2) the characterization of structures and properties of actinide and mixed actinide polymer materials; (3) the photochemistry of low-temperature uranium and plutonium systems, with particular interest on isotope effects and differences; (4) kinetic and thermodynamic studies of complexation and redox reactions in aqueous and nonaqueous systems; (5) determination of solvation numbers in aqueous and nonaqueous systems; (6) properties of complexes with macrocyclic ligands; (7) dissolution mechanisms of refractory metal oxides; (8) aqueous zirconium chemistry and redox ruthenium chemistry to establish chemical properties that determine separation and control of these fission products; and (9) studies of the fundamental properties of aqueous and nonaqueous solvent systems in support of these primary fields of investigation. Future plans include studies of catalytic effects of plutonium(IV) and uranium(IV) on actinide redox reactions, particularly the neptunium(VI → V → IV) reaction. [3.0 FTE]

**Chemistry Division** **$781,000**

### *136. Chemical and Structural Principles in Solvent Extraction*

*C.F. Baes, Jr., J.H. Burns, W.J. McDowell, B.A. Moyer*

This program uses a multifaceted approach to understanding the fundamental role of molecular structure and bonding in determining the chemical selectivity and physical properties of solvent extraction and related separation systems. Systematic surveys of a range of acidic, neutral, and basic extractants (individually and in synergistic combinations) are first carried out to identify promising systems. These are studied in detail to elucidate the thermodynamics of the reactions and the structures of their participants. Techniques used include: (1) extraction measurements as a function of the compositional variables to identify the reactions involved, (2) osmometry to determine the extent of association of various species in the organic phase, (3) calorimetric measurements to determine their heats and entropies of reaction, (4) x-ray diffraction of single crystals to determine molecular structure in solids, (5) NMR and FT infrared spectral measurements to determine the nature of bonding of species in solution and to correlate their molecular structures with those in solids, and (6) molecular mechanics calculations to evaluate relative energies of known and hypothetical species and predict stable configurations. The ultimate goal is to synthesize extractant molecules that will exploit the principles of extraction evolved through this work. [5.2 FTE]

## Pacific Northwest Laboratory
## Richland, Washington 99352

**Chemical Technology Department** **$945,000**

### *137. Analytical Mass Spectrometry Research*

*R.L. Gordon, J.M. Kelley, D.M. Robertson, J.J. Stoffel(s), R.A. Warner*

This program advances knowledge and techniques to extend the application of mass spectrometry to problems in chemical and isotopic analyses. The project (1) elucidates physicochemical mechanisms responsible for efficient ion production, (2) obtains methods for the control of surface work function of ion sources, (3) studies techniques for application of mass spectrometry to real-time analyses, and (4) establishes new ionization techniques. Surface analysis establishes physical and chemical properties of surface ionization sources and identifies chemical pathways responsible for ion production. Real-time mass spectrometry uses novel ion sources, mass separators, and ion detectors to develop direct particle sampling and measurement methods. Laser-assisted negative ionization is being utilized as a gentle technique for large organic molecules. [3.3 FTE]

### *138. 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 and thermodynamic constraints upon partitioning of a solute between a supercritical fluid and a condensed or supported phase. The project involves investigation of fluid-phase reactivities, solubilities, and phase-partitioning kinetics relevant to supercritical fluid chromatography and extraction phenomena. Phase partitioning and related chromatographic processes are being studied using direct fluid injection-mass spectrometry, classical equilibrium sampling, and solvatochromic techniques. The focus is on gaining an understanding of chromatographic processes for polar amd mixed supercritical fluid and solute systems and the kinetic and thermodynamic limitations upon separations in supercritical media. Both normal and reverse micelle systems, where the nonpolar phase is a supercritical fluid, are also being investigated as the potential basis for new separation methods. Experimental results are being compared with theoretical methods for prediction of fluid phase solubilities and actual chromatographic separations for model systems, to identify critical parameters for developing improved separation systems. [1.5 FTE]

### *139. Analytical Atomic Absorption Spectrometry Research*

*D.L. Styris, J.H. Kaye*

This project elucidates experimentally the mechanisms that control sample vaporization in furnace atomic absorption (FAA) spectrometry. Vaporization models obtained from these results provide understanding of chemical treatment and furnace effects, and thus establish the basis needed to help broaden and improve application of contemporary FAA spectrometric analysis. The neutral atoms, ions, and molecular species that appear in vapor phases during the temperature rise of the furnace are monitored simultaneously by atomic absorption and mass spectrometric techniques. Correlation of results from these experiments with furnace temperature and applications of chemical thermodynamic and kinetic data help to identify and characterize the controlling chemical and physical processes. Vitreous carbon, tantalum, and graphite furnace materials are being used in order to model the Group IIA element vaporization that occurs in presence of these furnace materials and the intragroup matrix modifiers. The experimental technique is also being used to verify theoretical models of vaporization (e.g., vaporization of aluminum and the influence of magnesium as a stabilizer) and to elucidate mechanisms responsible for interference in selenium measurements. [1.2 FTE]

### *140. Laser-Based Analytical Techniques*

*T.J. Whitaker, B.A. Bushaw, B.D. Cannon*

The objective of this project is to devise and evaluate ultrasensitive and highly selective laser-based analytical techniques for detection and measurement of trace substances related to energy production. Photon-correlation techniques have been obtained for several elements and sensitivities down to a few hundred atoms per cubic centimeter have been demonstrated. These techniques are applied to mixtures and compounds vaporized in an oven, to correlate the concentration in the vapor phase to the concentration in the bulk solid. In related work, photon-correlation techniques are studied to measure specific isotopes of noble gases. The extreme sensitivity and isotopic selectivity of photon-correlation spectroscopy may make it possible to detect ambient levels of these isotopes, thus providing an ideal atmospheric tracer and furnishing environmental monitoring for nuclear facilities. Techniques to efficiently excite noble gas atoms to the metastable state are being tested. The ability to efficiently produce metastables will not only permit photon-correlation measurements of noble gases but will also extend these measurements to several other elements that cannot currently be detected with this powerful technique. [1.2 FTE]

## Chemical Engineering Sciences

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

| Applied Science Division | $251,000 |
|---|---|

### *141. Turbulent Combustion*

*L Talbot, R.K. Cheng*

The interaction between turbulence and chemical reactions in premixed turbulent combustion flows is studied experimentally using laser diagnostic techniques and theoretically using vortex dynamics method. The objective is to obtain a better fundamental understanding of the turbulent combustion processes and to develop a theoretical model 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 by a stagnation plate. The flame structures in the reacting turbulent boundary layer have been characterized by a two-point Rayleigh scattering technique. A two-component LDA system has been used to study velocity statistics in the conical and stagnation flames. Spectral behavior of the velocity fluctuations in the v-flames has been analyzed. The Linear Array Rayleigh Scattering (LARS) system, which measures flow density simultaneously at 512 points, has been developed and will be used to study the dynamics of the flame front in the conical flame. A deterministic theoretical simulation of the v-flame based on the vortex dynamics method has been developed. The results compare well with the experimental data. Modeling of the conical flame and stagnation flame will be carried out. [2.2 FTE]

### Materials and Molecular Research Division $144,000

#### *142. 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 data toward reliable general prediction of phase equilibria for engineering. The correlations are expressed through semitheoretical physicochemical models in a form suitable for computer-aided design. Particular attention is given to systems of primary interest in energy-related industries, especially those concerned with fossil fuels, fossil fuel–water mixtures, and agricultural products. Since most high-boiling fossil fuel sources are mixtures of very many components, new experimental methods must be developed to determine the approximate composition of the mixture (characterization) and new conceptual tools must be developed to provide a framework for quantitative description of the mixture's properties (continuous thermodynamics). 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 $77,000

#### *143. Thermophysical Properties of Mixtures*

*J.J. Erpenbeck*

The thermosphysical properties of mixtures of particles interacting through the hard-sphere potential are evaluated, using the equilibrium techniques of Monte Carlo (MC) and molecular dynamics (MD), and nonequilibrium molecular dynamics (NEMD). The properties under investigation include both 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 appropriate numerical "experiments" seem appropriate. We also consider the merits of the various numerical techniques themselves in providing thermophysical properties. For the case of isotopic (mutual) diffusion, comparisons of the Green-Kubo and NEMD calculations have shown the methods to agree, yielding a mutual diffusion constant roughly 15% greater than the prediction of the Enskog theory, for a volume three-times close packing. The enhanced diffusion appears to arise from the existence of a long-time (perhaps $t^{-3/2}$) tail in the velocity–velocity time correlation function. The MC-MD study of the geometry of hard-sphere trajectories through the fractal dimension of the particle path in a many-particle fluid system has demonstrated the transition from mechanical motion for small length scales to Brownian motion at large length scales. It is found that for fluid densities the fractal dimension reaches the Brownian value of 2 only for length scales greater than 100 mean free paths. The hard-disk equation of state has been determined accurately for a wide range of fluid densities. The resulting values are found to be in excellent agreement with a "Levin" approximant to the virial series, including terms up to the sixth virial coefficient. [0.5 FTE]

## National Institute for Petroleum and Energy Research (NIPER)

### Bartlesville, Oklahoma 74005

### Processing and Thermodynamics Division $170,000

#### *144. Thermodynamic Characterization of Condensed-Ring Compounds*

*M.M. Strube*

Research continues on the thermodynamic characterization of condensed-ring organic hydrocarbons, as well as on organic oxygen, nitrogen, and sulfur compounds. Results are used from an experimental program that provides enthalpies of combustion, condensed-phase heat capacities for fluid-phase property behavior from very low temperatures and for third-law entropy determinations, vapor pressures, enthalpies of vaporization, vapor heat capacities, and molecular statistical thermodynamic properties for the ideal gases from Raman and infrared spectroscopy. The results are used to settle fundamental questions and to provide extensions to methods of prediction of thermodynamic properties from *ab initio* molecular orbital calculations and from semiempirical correlations based on molecular structure. Properties of concern include chemical thermodynamic properties (Gibbs energies, entropies, and enthalpies of formation) and thermophysical properties. The influence of heteroatoms, strain, and nonbonded intramolecular interactions are investigated, as is the influence of strong intermolecular interactions (e.g., hydrogen bonding, dipole interactions, molecular shape, internal bond strengths, and other conventionally recognized intermolecular forces). [3.0 FTE]

## Sandia National Laboratories

### Livermore, California 94550

### Thermofluids Division-8363 $231,000

#### *145. Analysis of Reacting, Turbulent Flows*

*W. Ashurst, A.R. Kerstein, J.Y. Chen, B. Sanders*

This research develops turbulence prediction methods for application to flows with high Reynolds numbers and large heat release. Four distinct modeling approaches are under study, each focused on a particular aspect of reacting turbulence: (1) time-averaged turbulence closure procedures, as these methods are still the most well-developed, and provide the best interpretation of turbulent diffusion flames; (2) unsteady vortex dynamics, a procedure that provides detailed flame propagation in premixed systems of complex geometry; (3) stochastic simulation of flame propagation, a new procedure that defines flame propagation by a process of random exchange between pockets of burned and unburned reactants; and (4) direct numerical simulation, where no turbulence approximations are used. Emphasis is on understanding the detailed mechanisms of heat, mass, momentum, and species transport in the mixing region of reacting flows. Our primary objective is to develop models of reactive turbulence that will be used to interpret data obtained in experimental reactive turbulence programs at the Combustion Research Facility, supported by the DOE Office of Basic Energy Sciences, Division of Chemical Sciences. [1.6 FTE]

# Heavy Element Chemistry

## Argonne National Laboratory
## Argonne, Illinois 60439

**Chemistry Division** **$1,280,000**

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

The heavy elements program is a long-range research effort to advance our understanding of the chemistry and physics of the actinide elements. Bonding and reactivity of actinides in key compounds and in solutions are probed by the systematic comparison of their properties (1) among several members of the 4f and 5f series, (2) in parallel oxidation states, or (3) in the same coordination sites. Emphasis is placed on the development of theoretical models that will aid in predicting the properties of unexplored systems. A well-focused effort in materials chemistry is designed to advance our knowledge of fundamental structure-bonding relationships and simultaneously to address more applied energy-related problems. The dynamic and thermodynamic parameters that characterize oxidation-reduction reactions of actinides in aqueous solutions are probed using state-of-the-art pulse radiolysis and stopped-flow methods. Such efforts help to define models that will be useful in predicting the behavior of actinides in process chemistry and in the aquatic environment. Efforts in spectroscopy, photophysics, and photochemistry are increasingly addressing higher valent reactive compounds of neptunium, plutonium, and americium, and are related to DOE programmatic interests in isotope separation. New opportunities are being exploited to broaden our understanding of electronic structure by focusing on the unique properties of curium, berkelium, and californium compounds. [10.0 FTE]

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

**Materials and Molecular Research Division** **$1,179,000**

### *147. 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]

## Los Alamos National Laboratory
## Los Alamos, New Mexico 87545

**Isotope and Nuclear Chemistry Division** **$255,000**

### *148. Actinide Chemistry in Near-Neutral Solutions*
*D.E. Hobart*

We are investigating a spectrophotometric method for determining the carbonate complexes of plutonium(IV) and their association quotients. The method involves competition between citrate and carbonate ligands for the plutonium. The research involves (1) the Pu(IV)–citrate system, (2) the mixed Pu(IV)–citrate/carbonate system, and (3) the Pu(IV)–carbonate system. Values for the formation quotients for the citrate complexes are available in the literature. We have found, however, that more than the two reported complexes exist in acid concentrations from 0.1 to 2.0 *M* at constant ionic strength. Experiments involving the carbonate systems are performed using solutions saturated with argon containing known partial pressures of $CO_2$ in order to fix the thermodynamic activities of carbon dioxide and carbonic acid. At least three carbonate-containing complexes have been deduced in the pH range from 7 to 9.5. Spectral data are taken at different wavelengths in the visible region. A nonlinear least-squares program has been adapted and is providing quantitative interpretation of the data. [0.8 FTE]

### *149. Actinide Organometallic Chemistry*
*A.P. Sattelberger, R.R. Ryan*

The project objective is to explore fundamental aspects of actinide organometallic chemistry. We are particularly interested in the synthesis, characterization, and reactivity patterns of three general types of early actinide (Th–Am) organometallic complexes. We study actinide(IV) monomers containing a single reactive site, e.g., (COT)(Cp)AnL, where L is a halide, pseudohalide, alkyl, or hydride ligand; COT is the cyclooctatetraene dianion; and Cp is the cyclopentadienide ligand. These complexes should provide new thermodynamic and mechanistic information on small molecule insertion chemistry without the complication of coupling reactions ubiquitous to the more extensively explored $Cp^*{}_2AnL_2$ complexes. We also study heterobimetallic complexes containing an actinide and a transition metal (or two actinides) held in close proximity by bridging ligands (e.g., phosphido, thiolato, or amido) or unsupported metal–metal bonds. The goal is to modify traditional reactivity patterns for the transition metals by the neighboring actinide's oxophilicity and Lewis acidity. The phosphido-bridged complexes prepared in our laboratory, e.g.,

$Cp^*_2Th(\mu\text{-}PR_2)_2Pt(PMe_3)$, have exhibited metal–metal bonding, and a systematic extension of this chemistry to other actinides is under current investigation. Finally, we study high valent (+5 and +6) organometallic complexes of the *trans*-thorium elements. High oxidation state organoactinide complexes offer the promise of enhanced reactivity not found in traditional An(IV) organometallics. We are currently investigating chemical and electrochemical routes to such species. [0.8 FTE]

### Materials Science and Technology Division $111,000

### *150. Actinide High-Temperature Thermodynamics*

*P.D. Kleinschmidt, J.W. Ward*

This research project measures the enthalpy and entropy of reaction of actinide compounds and gases by using the high-temperature gaseous effusion technique. The effort will concentrate on systems for which there are at present few measurements or for which the data appear to be unreliable. The systems include actinide fluorides, oxides, and oxyfluorides. A combination of precise second-law vapor pressure values with thermodynamic functions allows tabulation of heat capacity, heat content, and entropy data from 298 to 3000 K. The experimental results on the thermochemical stability of gases and solids will be correlated with the stability of other actinide and nonactinide systems. The thermochemical stability of these species is used to determine their concentrations in preparative reactions, purification, and photochemical processes. [0.8 FTE]

## Oak Ridge National Laboratory
## Oak Ridge, Tennessee 37831

### Chemistry Division $1,203,000

### *151. Chemistry of Transuranium Elements and Compounds*

*O.L. Keller, J.K. Gibson, R.L. Hahn, R.G. Haire, J. Halperin*

Studies are made in this project to enhance our understanding of the role of 5f electrons in chemical bonding. Most of our studies on the macroscopic scale emphasize certain isotopes available from the National Transplutonium Production Program centered at HFIR/TRU: ${}^{248}_{96}Cm$, ${}^{249}_{97}Bk$, ${}^{249}_{98}Cf$, ${}^{253}_{99}Es$, and ${}^{254}_{99}Es$. Particular classes of compounds, such as hydrides, chalcogenides, and pnictides are often selected for study on the basis of their utility in bringing out significant chemical differences between the lanthanides and the actinides. High-temperature/high-pressure experiments on actinide metals and compounds reveal characteristics about the degree of 5f electron localization as a function of atomic number in the series. Magnetic properties of metals and compounds are investigated using ultrasensitive methods and hydration numbers of ions in solution are investigated by neutron scattering at HFIR. As a result of a recently renewed multilaboratory effort involving four national laboratories, experiments are being formulated to investigate further the chemical properties of elements 101 to 105 on a "one-atom-at-a-time" basis. Since relativistic effects increasingly modify chemical behavior in heavier elements, ideas and calculations from relativistic quantum theory are employed to suggest experiments. Initial chemical methodologies to be applied in this latter work include solvent extraction, ion exchange, electrochemistry, and gas chromatography. Collaborative nuclear studies, primarily with targets of ${}^{254}Es$, are carried out with other national laboratories in efforts to discover new isotopes of elements 101 to 105 of utility in chemical experiments, or to improve the yields of known isotopes of these elements. [8.0 FTE]

# OFFSITE INSTITUTIONS

## Photochemical and Radiation Sciences

### University of Alabama
### Tuscaloosa, Alabama 35486

**152.** ***Magnetic Resonance and Optical Spectroscopic Studies of Radiation-Produced Radicals***
*L.D. Kispert* **$71,000**
*Department of Chemistry*

The objective of this research is to determine how the lattice affects energy transfer and primary radiation and photochemical processes in irradiated organic crystals and glasses. Such information is vital to understanding photosynthesis, photoinduced solid-state polymerization, electron and hole transport, and stereospecific reactions in solids. Electron spin resonance, electron-nuclear double resonance, electron-electron double resonance, and picosecond optical absorption techniques are used to identify the molecular fragments formed and to detect the energy transfer processes that occur. In particular, selected polyene, paraphenylene oligomers, sugar, carboxylic acid, and acetamide crystals are studied to determine the effect of host lattice on radical stability and reaction mechanisms as a function of temperature in crystals containing varying crystallographic forms. Preexisting electron traps, first observed by this research, have been studied in crystals of rhamnose and trehalose, radical intermediates have been identified in irradiated beta-carotene, the effect of carotenoids on the photoexcited triplet state lifetimes of porphines and the excited singlet lifetimes of carotenoids have been measured, and organic anions and cations have been detected and characterized.

### Alabama A and M University
### Normal, Alabama 35762

**153.** ***Photoacoustic-Laser Spectroscopy of Halogens and Mixed Halogens for Energy Purposes***
*P. Venkateswarlu* **$50,000**
*Department of Physics*

A photoacoustic spectrometer, including the electronic signal-averaging system, has been designed and fabricated, and a facility for simultaneous recording of the optogalvanic spectrum of neon/argon for wavelength calibration has been set up. The photoacoustic spectrum of iodine vapor in the presence of atmospheric air has been recorded in the region 4800 to 6000A. Recording of the high-resolution spectrum in the same region has been initiated. Work on similar lines will be continued on ICl, IBr, and $Br_2$. Further regular absorption and photoacoustic spectra will be recorded simultaneously to study the anomalies that might arise as a result of nonradiative relaxations to the neighboring levels or predissociations due to crossings by repulsive curves. The vertical positions of the high-lying repulsive states of the halogen molecules that dissociate into $^2P_{3/2} + {}^2P_{1/2}$ and $^2P_{1/2} + {}^2P_{1/2}$ atoms will be located by recording the photoacoustic spectra using the second harmonic of the tunable dye laser. This will establish the precise wavelengths of the solar radiation to be used for obtaining the halogen atoms in the $^2P_{1/2}$ state for the release of energy by transition to the ground $^2P_{3/2}$ state.

### University of Arizona
### Tucson, Arizona 85721

**154.** ***Mechanisms of Photochemical Energy Conversion by Chlorophyll***
*G. Tollin* **$93,400**
*Department of Biochemistry*

The goals of this project are (1) to elucidate the detailed mechanisms involved in light-induced one-electron transfer reactions involving chlorophyll (and related compounds), electron donors, and acceptors; and (2) to determine the interactions between the elementary steps in these processes and environmental parameters such as viscosity, dielectric constant, and homogeneous vs. heterogeneous reaction matrices. The intent is to develop a body of fundamental information that can be used to devise strategies for increasing the yields of the high energy products of such reactions, to physically separate these products and to decrease the probability of recombination (i.e., back reaction), and to facilitate secondary electron transfer to external donors and acceptors. Work involves the use of laser flash photolysis to monitor excited state and radical dynamics in lipid bilayer vesicle systems.

### Arizona State University
### Tempe, Arizona 85287

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

The adsorption of chlorophyll onto small particles of polyethylene that have been swollen with tetradecane provides the basis for developing a heterogeneous system for studying photochemical reactions. The absorption and fluorescence spectral properties of adsorbed chlorophyll, and the extent of its aggregation depend critically on the nature of other amphiphiles adsorbed with it, some of which may contain reducible groups and act as primary electron acceptors. Suspension of the particles in a viscous aqueous medium affords a stable two-phase system, in which chlorophyll-sensitized photochemical reactions take place at the interface where the pigment is located, and products are distributed into either phase, hydrocarbon or water, depending on their solubilities. The project objective is to detect and optimize reactions initiated by the chlorophyll singlet excited state, or by high-energy ion pairs derived from it. There is substantial evidence, on both kinetic and energetic grounds, for such reactions among the photoreductions of nitro compounds. Present emphasis on conventional photochemistry will be augmented by investigation of transient effects.

## Battelle–C.F. Kettering Research Laboratory
## Yellow Springs, Ohio 45387

### *156. Particulate Models of Photosynthesis*

*G.R. Seely* **$25,000 (5 mo.)**

The project consists of the investigation of photophysical and photochemical properties of chlorophyll, adsorbed together with other amphiphilic molecules on particles of polyethylene swollen with low molecular weight diluents. The swollen particles provide a viscous base for anchoring the hydrocarbon moieties of the amphiphiles, which helps protect chlorophyll excited states from dynamic quenching processes. The states of chlorophylls on these particles are especially characterized by their fluorescence spectra, quantum yields, and lifetimes, which depend on the amphiphiles adsorbed with chlorophyll. The present focus of our efforts is on the photochemistry of these particles suspended in an aqueous medium when various oxidants and reductants are added, especially those in which separation of products into different phases occurs, and on determining the nature of the excited states responsible for the reactions.

## Boston University
## Boston, Massachusetts 02215

### *157. Investigation of the Triplet States of Chlorophylls*

*R.H. Clarke* **$70,000**
*Department of Chemistry*

The characterization of the structures assumed by chlorophyll molecules upon aggregation in photosynthetic systems is important for an understanding of the mechanisms of energy conversion in photosynthesis. Since the properties of the excited triplet state of the pigment molecules such as the electron distribution and excited-state dynamics are sensitive to the surrounding interactions and to the state of aggregation, triplet-state properties serve as a convenient and nondestructive probe into the makeup of photosynthetic systems. Our present research project uses optical detection of magnetic resonance spectroscopy, Raman spectroscopy, and Raman-detected magnetic resonance to investigate the triplet-state properties of the chlorophyll molecule in lipid bilayers, in protein matrices, and as films deposited on surfaces. These measurements allow an evaluation of *in vitro* chlorophyll systems for structural features proposed as models for the antenna and reaction center of naturally occurring photosynthetic systems and for their general applicability as model systems for photosynthesis.

### *158. Study of Intermediates from Transition-Metal Excited-State Electron-Transfer Reactions*

*M.Z. Hoffman* **$77,000**
*Department of Chemistry*

Inter- and intramolecular electron-transfer reactions form the basis of most photochemical solar energy conversion processes. Excited states can be quenched via electron transfer, yielding oxidized and reduced species that are radicals or transition-metal coordination complexes in unusual oxidation states. The subsequent reactions of these species in homogeneous solution or at catalytic surfaces lead to the final products, which include high-energy materials capable of storage and use as a fuel. Steps in the overall process could involve intramolecular electron transfer between separated donor–acceptor sites contained in the same molecule. The ultimate yields of final, usable products depend on the efficiencies of the various reactions, which depend on the rates of the kinetically competitive steps. Because most of the species in an aqueous environment are ionic, the extent of ion pairing and aggregation of the reactive species has a dramatic influence on the rates of the mechanistic steps. This research, which has used the techniques of continuous and pulsed photolysis and radiolysis, has focused on the following aspects of excited-state electron-transfer reactions involving coordination complexes and ion-pair donor–acceptor complexes to understand the parameters that govern the reaction pathways in the photochemical processes: (1) ion pairing and aggregation among reactive species; (2) control of the yields of redox products; (3) chemistry of reaction intermediates; (4) properties of excited states of polypyridyl complexes; and (5) mechanisms of intramolecular electron transfer.

### *159. Photoinduced Electron Transfer in Ordered Structures*

*G. Jones* **$96,000**
*Department of Chemistry*

This research is directed to the study of photoinduced electron transfer reactions that occur in homogeneous solution. In order to develop new electron or hole relays of potential importance in photoredox processes, a study of novel sulfur heterocycles has been completed. These compounds are capable of transfer of latent oxidation equivalents (two equivalents per molecule of carrier), a relay machanism that was deployed in the photosensitized oxidation of halide ion. A parallel study of electron relays involved a comparison of a series of pyridinium ions with the well-known electron acceptor, methyl viologen. The capability of the pyridiniums for quenching a Ru(II) sensitizer and for photoformation of hydrogen from water was assessed. The photochemistry of a series of charge-transfer complexes of ion pairs of methyl viologen was also studied. These complexes involved electron donors such as aromatic amines, naphthalenes, dicarboxylate ions, and polycarboxylates. A novel wavelength dependence on the yield of net electron transfer for these complexes was found and studied in detail. The quinone electron acceptor, chloranil, was investigated in combination with electron donors such as methylated benzenes, conjugated dienes, and benzhydrols. The mechanisms of electron transfer for these systems were studied with particular attention paid to a comparision of coupled electron transfer, proton transfer processes. Differences in reactivity were observed for reactions proceeding via chloranil triplet and reactions initiated by irradiation of chloranil ground state complexes. Another study probed the photophysics and electron transfer photochemistry of triarylmethane dyes that are bound in aqueous solution to polyelectrolytes. Evidence was obtained for long-range energy and electron transfer for aggregated dye counter-ions.

## Brandeis University
## Waltham, Massachusetts 02254

### *160. Photochemical Reactions of Complex Molecules in Condensed Phase*

*H. Linschitz* **$88,700**
*Department of Chemistry*

This project seeks to identify and evaluate factors governing the efficiency of primary radical formation in excited-state redox reactions. This is a general problem confronting photochemical energy conversion since the same kinetic intermediates involved in energy-storing charge separation lead also to dissipative quenching. Radical yields are measured by laser flash photolysis on donor–acceptor systems in solution, using aryl ketones and porphyrins as substrates. In reduction of triplet ketones by simple anions, marked increases in radical yields are found as anion concentration is increased far above quenching levels. Kinetic studies and experiments with mixed halide systems establish that this results from reaction of the primary triplet charge-transfer exciplex with excess anion, to form a composite complex with decreased spin-orbit interaction. As models of photosynthetic reaction centers, ion-paired porphyrin aggregates have been prepared from oppositely charged monomers. In solution, equilibria strongly favor dimer species, whose spectra, emission yields, magnetic properties, and triplet lifetimes have been characterized. Mixed dimers containing different metals show biphasic decay of flash transients suggesting charge transfer within the triplet excited ion pair.

## University of California
### Irvine, California 92717

### *161. Research in Chemical Kinetics*
*F.S. Rowland* **$190,000**
*Department of Chemistry*

This project focuses on understanding the rates and mechanisms of chemical reactions, including some of interest to atmospheric chemistry. The reactions of thermalized $^{18}F$ and $^{38}Cl$ atoms with gaseous $(CH_2{=}CHCH_2)_4M$ compounds are studied for M = tin, germanium, silicon, carbon to determine the extent of restricted intramolecular energy flow (non-RRKM) in such systems. Reactions of halogen atoms with haloolefins ($X + CH_2{=}CHY$; X = fluorine, chlorine; Y = fluorine, chlorine, bromine, $CH_2Cl$) furnish rate information about radical lifetimes, and mechanistic information such as selectivity and isomerization. The temperature dependence of $^{38}Cl$ reactions with olefins is studied over the 240 to 360 K temperature range. Rate constants for hydrogen abstraction reactions by $^{38}Cl$ are studied over this temperature range by their competition with olefin reactions. The mechanism of the direct gas-phase photolysis of $^{14}CS_2$ is investigated with and without $O_2$ present. The rates and mechanisms of hydrolysis in aqueous solution are measured for gases occurring in the atmosphere, including OCS, $CH_3I$, and $CH_3Br$. The gas-phase photolyses of $PH_3$ and $P_2H_4$, and the co-photolysis of $PH_3$ and $NH_3$ are investigated. The thermalization of energetic tritium atoms in collisions with krypton and $CF_4$ is studied using the additional reaction with $C_2H_4$ as the monitor.

### *162. Single-Collision Studies of Hot Atom Energy Transfer and Chemical Reaction*
*J.J. Valentini* **$61,200**
*Department of Chemistry*

This project involves the study of the dynamics of reactive and inelastic (energy transfer) collisions of translationally hot hydrogen, deuterium, and oxygen atoms. The hot hydrogen, deuterium, and oxygen are produced by pulsed-laser photodissociation of appropriate precursors (e.g., HI and DI for hydrogen and deuterium atoms, and $O_3$ for oxygen atoms). Photochemical sources (precursors) for these and other translationally hot atoms are being developed and characterized. Photofragment spectroscopy is used to determine the translational energy of the atom as a function of photolysis wavelength. The reactive and energy transfer collisions of these translationally hot species with molecules like $N_2$, $O_2$, CO, $CO_2$, $NH_3$, $CH_4$, $CF_4$, and $SF_6$ are being investigated. By variation of the hot atom precursor and the wavelength of photolysis of the precursor, we select the hot atom translational energy in the range of a few tenths to several eV. We measure the rotational and vibrational distributions of the reactive or energy transfer product under single-collision conditions using highly time-resolved coherent anti-Stokes Raman scattering spectroscopy. These measurements yield the state-to-state cross sections for the hot atom collisional processes, and by simple calibration procedures, the total cross sections as well. The objective of this research is to elucidate the dynamics of hot atom collisions, and to contribute to the development of theoretical models of these processes.

## University of California
### Los Angeles, California 90024

### *163. Time-Resolved Laser Studies on the Proton Pump Mechanism of Bacteriorhodopsin*
*M.A. El-Sayed* **$115,000**
*Department of Chemistry and Biochemistry*

Bacteriorhodopsin (BR) is the other photosynthetic system besides chlorophyll. While chlorophyll uses an electron pump to store energy, BR uses a proton pump. The understanding of storing solar energy via proton pumps is of vital importance. Thus the understanding of the primary photochemical and photophysical process in BR is of vital current interest. We developed time-resolved resonance Raman and optical techniques to record the spectra of the different transients formed following the initial photosynthetic absorption process. We investigate (1) whether energy migration takes place to specific sites prior to photochemistry; (2) whether isomerization of retinal takes place on the picosecond time scale; and (3) how the Schiff base loses its proton during the photochemical cycle. Time-resolved optical spectroscopy of the protein and retinal systems is used to identify the nature of coupling between these two systems, which is undoubtedly responsible for the proton pumping required for photosynthesis in bacteriorhodopsin.

## University of California
### Santa Barbara, California 93106

### *164. Energy Transformations in Transition Metal Complexes*
*R.J. Watts* **$138,000**
*Department of Chemistry*

This project explores basic photochemical and photophysical phenomena in transition metal complexes. The primary areas of endeavor include: (1) photochemical and photophysical consequences of metal–carbon bonding to acceptor ligands with extended $\pi$ systems; (2) electronic relaxation phenomena between excited-states of metal complexes; (3) mechanisms of excited-state electron transfer reactions; (4) tuning of electronic excited states by extension of $\pi$ conjugation in N-heterocyclic ligand–metal complexes; and (5) photophysics of mixed-valence solid-state materials. Techniques applied in these projects include time-resolved emission spectroscopy, laser-induced transient and excited-state absorption spectroscopy, and $^1H$ and

$^{13}C$ NMR spectroscopy. Laser double resonance techniques are presently being developed with newly acquired excimer/dye lasers for the purpose of characterizing electronic relaxation between excited states of metal complexes. Synthesis and characterization of complexes containing metal–carbon bonds are carried out to facilitate the projects in area (1) above. The emission spectroscopy and photoinduced electron-transfer reactions of several of these complexes show them to be powerful photoreducing agents. Their participation in photoinduced electron-transfer reactions that are highly endergonic are presently under investigation.

## Clemson University
## Clemson, South Carolina 29634

### *165. Intramolecular Energy Transfer Reactions as a Method for Metal Complex Assisted Production of Hydrogen*

*J.D. Petersen* **$76,600**
*Department of Chemistry*

Current research concentrates on coupling highly absorbing metal centers to potentially photoactive metal centers (e.g., metal dihydrides) by covalent bonding through bridging ligands. This is done in order to use low-energy light to drive useful chemical reactions by intramolecular energy transfer processes. Energetically, this process is feasible. Irradiation of a visible-light absorbing iron complex at 577 nm in the presence of a nonabsorbing cobalt–dihydride complex leads to sensitization and the formation of molecular hydrogen. Current efforts concentrate on covalently coupling iron and ruthenium to cobalt and rhodium systems. Additional studies involve preparation of a new, highly absorbing, photoluminescent metal center, $Ru(dpp)_3{}^{+2}$, where dpp = 2,3-bis(2-pyridyl)pyrazine. The complex will bind other metal centers to form tetrametallic clusters such as $Ru[(dpp)Ru(bpy)_2]_3{}^{8+}$. These clusters have excited-state properties associated with the core metal center and redox chemistry characteristic of the peripheral metal centers.

## University of Colorado
## Boulder, Colorado 80309

### *166. Chemical Probes of Charge Transfer at Semiconductor/Liquid Junctions*

*C.A. Koval* **$69,900**
*Department of Chemistry and Biochemistry*

Fundamental aspects of heterogeneous charge transfer kinetics at certain semiconductor-solution interfaces will be investigated to improve efficiencies and lower costs of devices based on photoelectrochemical cells. Electron transfer processes at p-InP and n-InP electrodes of high to moderate doping density were investigated by monitoring the cyclic voltammetric (CV) dark currents of a series of metallocenes in acetonitrile solutions. The formal reduction potentials of ($E^{o\prime}$) of the metallocene +/0 couples span the band gap of InP, allowing a comparison of the CV responses as a function of $E^{o\prime}$ and the energetic condition of the electrode surface. The energetic condition of the electrode surface during the CV experiments was monitored by measurements of the capacitance of the space charge region. CV behavior at InP was dependent on three factors: (1) the doping density of the electrode, (2) the formation of surface oxide during the experiment, and (3) the proximity of $E^{o\prime}$ to either the conduction or valence band edge.

## Columbia University
## New York, New York 10027

### *167. Laser-Enhanced Chemical Reaction Studies*

*G.W. Flynn* **$106,000**
*Department of Chemistry*

This project is a study of chemical reactions of laser-pumped molecules, with particular emphasis on the role of vibrational energy transfer processes in chemical dynamics. Fast hydrogen, chlorine, and deuterium atoms are produced by pulsed excimer laser photolysis of gaseous diatomic molecules. These medium-hot atoms cause vibrational excitation of stable molecules during collisions, or react chemically to form products inaccessible to thermally cold species. An infrared diode laser probe technique developed specifically for this project is used to monitor, with a resolution of milliwavenumbers, the precise vibrational and rotational states excited during such collisions. The extraordinary resolution of this probe method provides previously unavailable details and insights concerning fundamental combustion, photochemical, and collision processes. Chemical reactions between $CO_2$ and hot hydrogen atoms, between CO and OH, and between $CO_2$ and oxygen atoms are investigated, along with photodissociation of small organic acids.

## Dartmouth College
## Hanover, New Hampshire 03755

### *168. Photoexcited Charge Pair Escape and Recombination*

*C.L. Braun* **$84,700**
*Department of Chemistry*

The escape and recombination of charge pairs produced by photoexcitation of organic molecules is studied. The recombination of geminate charge pairs formed by the photoionization of solute molecules in low dielectric constant solvents occurs in picoseconds. This process is studied by pump-probe conductivity techniques. The conductivity measurements are compared with picosecond absorption measurements of the recombination kinetics. The data are analyzed with a detailed theory of the diffusive recombination of geminate charge pairs. The charge pairs are found to undergo Brownian motion in the coulomb well before recombining or separating; no hot electron effects are observed. The second key goal is to understand the mechanism of charge pair escape in electronically excited electron donor–acceptor materials. A number of donor–acceptor geometries are explored in these solid-state studies. The possible role of the lowest energy charge transfer state in the formation of separated charge pairs (current carriers) is of special interest. Steady-state and nanosecond pulse measurements of both photocurrents and fluorescence are used to test mechanistic ideas.

## University of Florida
## Gainesville, Florida 32611

### *169. Radiation Chemistry of Hydrocarbon and Alkyl Halide Systems*

*R.J. Hanrahan* **$79,000**
*Department of Chemistry*

This research is directed towards understanding the mechanism of product formation in gamma or pulsed electron radiolysis of simple chemical systems. Measurements have been made on the rates of reaction of OH free radicals with aliphatic and aromatic hydrocarbon gases, and with simple fluorocarbons, using the method of argon-sensitized pulse radiolysis. Analysis of the rate data using computer simulation with a Gear integrator is in progress. Rates of OH loss in systems containing only water and argon are consistent with current literature values of OH + OH and OH + H rate constants, provided the extinction coefficient for OH absorption at 309.5 nm is taken as $6.39 \times 10^4$ liter/(mole cm). Formation of difluorocarbene has also been measured in several systems. An investigation of the radiolytic oxidation of propane has shown many similarities to thermal oxidation, in both products and reaction pathways. This work is being extended to normal butane, and further analysis of the data is in progress. Data on the effect of added nickel catalyst and on oxygen-containing products in the radiolysis of $H_2$–CO mixtures is being prepared for publication.

## University of Houston
## Houston, Texas 77004

### *170. Charge Separation in Photoredox Reactions*

*L. Kevan* **$195,000**
*Department of Chemistry* **(24 mo.)**

The objective of this research is to probe the molecular mechanistic and structural aspects of charge separation in photoredox reactions in micellar and vesicle systems in order to eventually couple this charge separation to chemical energy storage. Tetramethylbenzidine has been photoionized to produce the cation radical in liquid and frozen micellar solutions, and the photoionization mechanism has been contrasted in anionic and cationic micellar systems. The cation is observed by optical absorption, electron spin resonance, and electron spin echo spectrometry. Nitroxide–water and nitroxide–surfactant interactions, detected by electron spin echo modulation analysis, with specific deuteration indicate how the surfactant conformation is related to the photoionization efficiency. Micelle surface modification by varying counterions has led to some control of surfactant conformation. The decay kinetics of photoproduced cations in micelles are characterized by time-dependent rate constants, and the associated activation energy distributions have been determined.

## Louisiana State University
## Baton Rouge, Louisiana 70803

### *171. Theoretical Studies of Electron and Proton Transfer Processes in Fluids*

*N.R. Kestner* **$120,000**
*Department of Chemistry* **(24 mo.)**

This research project is designed to study electron and proton transfer processes in fluids, especially those that could be important in energy conversion. General theoretical studies probe the role of temperature, pressure, and solvent effects on electron transfer rates. Special attention is directed to such effects for reactions in the abnormal, or highly exothermic regions. The general theories are applied to specific reactions. In this regard, we are determining very accurate water–water interactions and other intermolecular potentials, exploring in detail the role and elimination of basis set errors. These are used to obtain accurate interaction energies between electron transfer species such as iron(II) and iron(III) in aqueous solutions. Other studies are directed at predicting electron transfer rates in glasses and highly viscous media using statistical mechanical methods as well.

## Marquette University
## Milwaukee, Wisconsin 53233

### *172. Resonance Raman and Photophysical Studies of Polypyridine Complexes of Ruthenium*

*J.R. Kincaid* **$100,000**
*Department of Chemistry* **(6 mo.)**

The project objective is to investigate the effects of selective chemical modification on the electronic structure and dynamics of excited states of metal diimine complexes. The approach involves the synthesis and thorough characterization of excited-state photophysical and photochemical processes for complexes comprised of various bipyridine derivatives and related ligands. The ground- and excited-state vibrational spectra are obtained using resonance Raman, time-resolved resonance Raman, and conventional infrared spectroscopies. The spectra are interpreted with the aid of carefully developed normal mode analyses to identify and characterize the lowest lying $^3$MLCT states, thereby providing a basis for structural interpretation of excited-state dynamics. These studies will provide valuable guidelines for synthetic control of excited-state properties and may ultimately aid in rational design of energy conversion devices.

## University of Massachusetts
## Boston, Massachusetts 02125

### *173. Investigation of the Structure of Photosynthetic Reaction Centers*

*H. van Willigen* **$74,300**
*Department of Chemistry*

The structure of photosynthetic reaction centers and model systems is studied with the aid of magnetic resonance techniques and optical spectroscopy. Research focuses on the effect of porphyrin dimerization on the characteristics of the optical absorption and emission spectra, and on the ESR spectra of the photoexcited triplets. Systems investigated include anionic and cationic tetraphenyl porphyrins (TPP), and TPPs with crown ether substituents. An ENDOR study is under way on the monomer and dimer of the Cu(II) substituted crown ether porphyrin, to characterize the geometry of the dimer, which has a triplet ground state.

## Massachusetts Institute of Technology
## Cambridge, Massachusetts 02139

### *174. Photochemical Energy Storage: Studies of Inorganic Photoassistance Agents*
*M.S. Wrighton* **$250,000**
*Department of Chemistry*

Light-driven, energy-storing chemical reactions are the object of study in this research project. Emphasis is on the use of chemically derivatized semiconductor electrodes and macromolecular redox/absorber systems as the photoassistance agents for redox reactions such as the oxidation and reduction of $H_2O$. Fundamental studies of the nature of semiconductor–electrolyte interfaces to establish the energetics and kinetics for light-driven redox processes are one aspect of the project. Another aspect is chemical derivatization of the semiconductor surface to improve durability and kinetics for the desired redox reaction. In the area of electrocatalysis, surface modification with metals, oxides, and polymers is being studied. Catalysis of halide oxidation and $H_2O$ reduction have received most attention. Catalytic materials include noble metals, oxides, and molecular catalysts. Exploratory studies to find unique interactions of redox reagents with semiconductor electrode surfaces, such as S-donors with II–VI semiconductors, are in progress. Such unique interactions lead to high efficiency for energy conversion and specific redox processes.

## University of Minnesota
## Minneapolis, Minnesota 55455

### *175. The Contribution of Electronically Excited States to the Radiation Chemistry of Organic Systems*
*S. Lipsky* **$81,600**
*Department of Chemistry*

We study photophysical properties of organic molecules that have relevance in determining their behavior when subjected to ionizing radiation. Significant recent advances include: (1) observation and quantification of the effect of a scavenger to reduce the average range of an electron photoejected into a nonpolar liquid via its interaction with the electron prior to thermalization; (2) measurement of the dependence on excitation energy of the photoionization quantum yield and electron thermalization range of solutes in nonpolar liquids, and the observation of a structure in these spectra that can be attributed to the production of electronically excited states of the molecular ion; (3) observation and quantification of the effect of small concentrations of cyclic perfluorocarbons to enhance photocurrent production from certain solutes in certain nonpolar fluids, thereby enhancing ionization effects in these systems; (4) observation of contact charge transfer absorption maxima between saturated hydrocarbons and perfluorocarbons, and application to determination of relative electron affinities of various perfluorocarbons; and (5) observation and quantitative measurement of fluorescence yields and fluorescence spectra from certain highly strained cycloalkanes not previously observed to emit. The high sensitivity of these yields to changes in strain energy provides an improved technique for determining how the strain is affected by small structural perturbations.

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

### *176. Reference Data in Support of Energy Programs*
*D.R. Lide, Jr.* **$70,000**
*Office of Standard Reference Data* **(24 mo.)**

The Office of Standard Reference Data of the National Bureau of Standards administers a collaborative interagency program for the preparation of compilations of physical and chemical reference data. Current projects within the scope of the Division of Chemical Sciences fall in the following areas: physical and thermodynamic properties of fluids, solubility, electrolyte properties, gas-phase chemical kinetics, hydrocarbon properties, atomic data relevant to fusion, and thermodynamics of high-temperature systems. The approach is to review critically all relevant data from the literature, compare with theory, and select the most reliable values. Whenever possible, correlations are developed that allow prediction of unmeasured properties. Reviews have recently appeared or are in press on high-temperature vaporization of alkali metal oxides, nucleation limits of liquids, thermodynamic properties of ethylene, solubility of toxic polyaromatic hydrocarbons, and other topics.

### *177. Pulse Radiolytic Studies of Inter- and Intramolecular Electron Transfer Processes*
*P. Neta* **$134,000**
*Center for Chemical Physics*

Studies of electron transfer processes are conducted using pulsed electron sources to generate the reactive intermediates and time-resolved absorption spectrophotometry to follow the kinetics of the ensuing reactions. These studies involve organic and inorganic radicals and unstable oxidation states, mostly in aqueous solutions, and concentrate on the kinetics, thermodynamics, and mechanisms of their reactions. The main objective of this work is the study of electron transfer reactions of metalloporphyrins that may be applicable to solar energy conversion systems. These include one-electron reduction or oxidation to radical anions or cations or to unstable oxidation states, and the subsequent reactions of the resultant species. Emphasis is given to reactions of these species with catalysts that may lead to decomposition of water to hydrogen and oxygen. These studies are concerned also with kinetics and mechanisms of reactions of metalloporphyrins with various radicals. Studies on simple organic and inorganic radicals are aimed at understanding the mechanisms of their reactions and determining the basic properties of these species, such as redox potentials and rates of self-exchange. Intramolecular interactions are studied in several systems and attempts are made to monitor rates of intramolecular electron transfer in specially designed molecules, derived mainly from viologens and metalloporphyrins.

## University of Nebraska
## Lincoln, Nebraska 68588

### *178. Electrochemical and Optical Studies of Model Photosynthetic Systems*
*T.M. Cotton* **$80,000**
*Department of Chemistry*

A combination of electrochemical and resonance Raman techniques, supplemented by ultraviolet-visible spectroscopy, is used to characterize important properties of the pigments of the bacterial photosynthetic reaction center. Characterization includes (1) determination of the redox states of the various components involved in the initial photoact and (2) identification of the spectral properties of the neutral and charged species. Much of the present knowledge of the primary photoact in photosynthesis is based on *in vitro* or *in vivo* measurements, which are subject to ambiguous interpretation. The present approach uses innovative techniques in an attempt to overcome some of the drawbacks of previous studies. Efforts are under way to incorporate bacteriochlorophyll, bacteriopheophytin, and quinones from reaction centers into monolayer arrays. In these defined monolayer constructions the orientation, spacing, and identity of the included components are under a high degree of control. Therefore, photoinduced electron transfer will occur in highly defined systems. Electrochemical and spectral studies of the monolayer systems should provide new insights regarding the effect of structure on the optical and redox properties of these molecules.

### *179. Energetics of the Formation and Reactions of Gaseous Ions*

*G.G. Meisels* **$90,000**
*Department of Chemistry*

We study the unimolecular dissociation of gaseous ions whose internal energies are known within 0.025 eV, using threshold photoelectron-coincident photoion mass spectrometry as the major experimental approach. Supporting information is obtained from studies of collision-induced fragmentation in a triple sector mass spectrometer, with the collision chamber inserted between the second and third stages. The applicability of statistical or state-selected models to describe dissociation pathways is assessed on the basis of data on ionization and fragmentation threshold and energetics, ion lifetimes with respect to dissociation in the millisecond to microsecond range, kinetic energy release accompanying fragmentation, and isotope effects on these. Methylformate fragments to methanol ion via two processes at rates much slower than expected from statistical theory, while dimethylsulfoxide fragments entirely statistically. Accurate ion energetics were reported for the first time on this molecule; all onsets are substantially lower than estimated previously.

### *180. High Energy Halogen Reactions Activated by Nuclear Transformations*

*E.P. Rack* **$80,500**
*Department of Chemistry*

The functional goal of this project is to understand better the chemical reactivity of high-energy monovalent species. High-energy reactions of halogen atoms or ions activated by nuclear transformations are studied in gaseous, high-pressure, and condensed-phase saturated and unsaturated hydrocarbons, halomethanes, and liquid and solid aqueous solutions of biological molecules. Specifically, the stereochemistry involving single chiral center molecules, systematics, mechanisms, and halogen reactivity in a collapsing molecular environment, and caging of hot atoms in an ice lattice are under investigation. The stereochemistry of exothermic halogen atom homolytic bimolecular substitution ($^{S}H^{2}$) at the chiral centers of chiral 2-halopropionyl halides is currently studied. Practical applications of recoil atom chemistry to activation analysis for molecules in biological or environmental systems, to radiopharmacy involving synthesis and radioprotection, and to the study of solute–solute and solute–solvent interactions of dilute aqueous solutions of methyl halides and biological molecules are carried out.

## University of North Carolina
## Chapel Hill, North Carolina 27514

### *181. Energy Conversion Processes Based on Molecular Excited States*

*T.J. Meyer* **$106,000**
*Department of Chemistry*

The project objective is study, design, and exploitation of excited states of transition-metal complexes in energy conversion applications. Work involves: (1) measurement of the photochemical and photophysical properties of excited states; (2) application of theory to such processes; (3) synthesis of new types of potential photosensitizers; (4) preparations and properties of metallopolymers containing metal complex chromophores and chromophore-quencher combinations; (5) study of electron- and energy-transfer processes of the photosensitizers in solutions, soluble polymers, and polymeric films; and (6) possible applications of these materials in photochemical and photoelectrochemical energy conversion processes.

## University of North Carolina at Charlotte
## Charlotte, North Carolina 28223

### *182. Oligomer and Mixed-Metal Compounds, Potential Multielectron Transfer Catalysts*

*D.P. Rillema* **$66,200**
*Department of Chemistry*

The goal of the project is to design and characterize new classes of photosensitizers and their application to solar energy conversion. Current work involves characterizations of fundamental precursors that will be used (1) to prepare molecules that contain a coordinatively unsaturated metal complex connected to a photoactive electron transfer metal chromophore and (2) to synthesize multimetal complexes capable of simultaneous multielectron transfer. The characterizations include: (1) isomer separation of metal complexes containing asymmetric ligands; (2) thermodynamic studies of ground-state and excited-state redox properties; (3) assessment of the relative energy positions of heterocyclic ligand $\pi^*$ energy levels and their exploitation for the preparation of new light-sensitive chromophores; and (4) photophysical investigations of the excited-state energies, lifetimes, and electron transfer properties of the photochromophores.

## Oregon Graduate Center
## Beaverton, Oregon 97006

### *183. Fundamental Studies in Charge Separation at Interfaces in Relation to Water Photolysis*

*J.K. Hurst* **$100,000**
*Department of Chemical, Biological and Environmental Sciences*

This project aims to improve our conceptual understanding of the influence of microphase separation and compartmentation upon oxidation-reduction processes. Three aspects are considered, all of which are essential to developing practical "wireless" devices for solar photoconversion: (1) use of interfaces to promote charge separation and increase lifetimes of the initial redox products, (2) identification of mechanisms of transmembrane redox across bilayer membranes, and (3) development of regenerative cycles for water photolysis. We have developed systems for Zn(II) porphyrin photoreduction of N-alkyl-N′-methylbipyridinium(II) ions at the highly negatively charged interfaces of dihexadecylphosphate (DHP) vesicles with unprecedentedly high quantum yields (i.e., greater than 0.95) for formation of charge-separated products. The dissipative recombination reactions are strongly retarded by electrostatic repulsion, allowing opportunity for coupling to following reactions leading to net photoconversion. Two redox systems have been developed that exhibit apparent electron exchange between components bound at the opposite interfaces. With DHP-bound viologens, kinetic studies have provided evidence that binding is heterogeneous and that transmembrane redox can occur only from certain presumably buried sites. Structural characterization by several techniques is currently under way. Finally, chemical characterization of new dimeric ruthenium $\mu$-oxo ions isolated from complex product mixtures has been initiated. These studies are prompted by observations that the crude product is capable of efficiently catalyzing water oxidation in the presence of suitable strong oxidants.

## Pennsylvania State University
## University Park, Pennsylvania 16802

### *184. The Free-Radical and Ion Chemistry of Volatile Silanes, Germanes, and Phosphines*
*F.W. Lampe* **$160,000**
*Department of Chemistry* **(24 mo.)**

This research project consists of experimental studies of the chemical reactions initiated by the irradiation of gaseous silanes and germanes with electrons, infrared laser radiation, and vacuum-ultraviolet light. From the experimental studies, fundamental reaction mechanisms relative to this new and unexplored chemistry are developed. In particular, the understanding developed enables us to attempt useful exploitations of photochemical and radiation chemical techniques for the synthesis of amorphous solids of silicon, germanium, and mixtures thereof. Presently under study is the infrared laser photochemistry of $SiH_4$–$D_2$, $SiH_4$–NO, $SiH_4$–$GeH_4$, and $SiH_4$–$CH_3Cl$ mixtures; the vacuum-ultraviolet photochemistry of $GeH_4$ and $SiH_4$–$GeH_4$–NO mixtures; and the ion chemistry of $SiH_4$–$CH_3Cl$, $SiH_4$–$CH_2Cl_2$, $SiH_4$–$CHCl_3$, $SiH_4$–$CCl_4$, and $CH_4$–HCN mixtures.

## Princeton University
## Princeton, New Jersey 08544

### *185. Surface Chemistry at the Semiconductor–Electrolyte Interface*
*A. Bocarsly* **$76,800**
*Department of Chemistry*

This study encompasses the role of surface chemistry in photodecomposition processes occurring at the II–VI semiconductor–electrolyte interface. Both anodic and cathodic decomposition channels in n-cadmium chalcogenide-based systems are of interest. Recent work has focused on the surface chemistry of n-CdS and n-CdSe photoelectrodes in a $Fe(CN)_6^{4-/3-}$ electrolyte. Illumination of such interfaces produces a layer of $[Cd^{II}Fe^{III}(CN)_6]^-$ on the electrode surface. This overlayer has a zeolytic structure and ion exchange properties that allow the facile transport of alkali cations. Iron sites in this layer are electroactive ($Fe^{II/III}$) and support mediated charge transfer from the semiconductor to solution $Fe(CN)_6^{4-/3-}$. This process is intimately coupled to the flow of supporting cations through the surface layer. The nature of the intercalated cation strongly affects the energy distribution of redox states in the surface layer. Thus, the semiconductor/overlayer interfacial energetics (and kinetics) can be maximized by appropriate choice of the alkali cation. In the case of n-CdS/$Fe(CN)_6^{4-/3-}$ cells, this is accomplished by the addition of $Cs^+$. Such cells not only show dramatically improved stability, but yield monochromatic optical-energy conversion efficiencies (488 nm) in excess of 20% with fill factors of ~ 65%. This represents a threefold improvement over previously reported n-CdS-based photoelectrochemical cells.

### *186. Metalloporphyrins as Energy-Transfer Catalysts*
*T.G. Spiro* **$186,000**
*Department of Chemistry* **(24 mo.)**

The electrochemistry and photoelectrochemistry of metalloporphyrin electrode films are explored, with a view toward catalyzing useful energy storage reactions, including the splitting of water to $H_2O_2$. Stable metalloprotoporphyrin films have been prepared via electroinitiated polymerization of the vinyl sidechains, and other porphyrin polymerization schemes are under investigation. Cobalt porphyrins are applied to the catalysis of $H_2$ production from water. The kinetics of the catalysis have been investigated in homogeneous solution using electrochemical techniques. Cobalt porphyrin electrode films capable of sustained $H_2$ production have been developed, and their characteristics are studied. Iron, chromium, and manganese porphyrins are explored in oxidative chemistry, with the eventual aim of catalyzing water oxidation.

## University of Rochester
## Rochester, New York 14627

### *187. Picosecond Studies of Charge Transfer at Semiconductor Liquid Junctions*
*R.J.D. Miller* **$76,800**
*Department of Chemistry*

The advent of efficient semiconductor liquid junction solar cells provides an excellent system for *in situ* spectroscopic studies of the electron or hole (charge) transfer process at solid–liquid interfaces. The ultrafast kinetics of the interfacial transfer process are not well understood. To date, there have been two proposed mechanisms for the photoinduced charge transfer step: (1) tunneling processes across the space charge region (Helmholtz barrier) and (2) thermally equilibrated charge scattering from the surface. The predicted time course for these two mechanisms is (respectively) ~100 fsec and > 10 psec. Two techniques, picosecond holography and a proposed new method of electrooptic sampling, will be used to optically study the photoinduced charge transfer process directly at the semiconductor–liquid interface. The observables of the two techniques are the charge transfer rate (via the minority carrier lifetime) and the temporal behavior of the electric field across the space charge region, respectively. Both techniques have adequate temporal resolution (~100 fsec) and sensitivity to distinguish on the basis of the observed time scale, which mechanism, if either, is operating for a particular system. Studies will focus on understanding the effect of the depletion layer width and the effective mass of the minority carrier on the charge transfer dynamics.

### *188. Applications of Photoinduced Electron Transfer and Hydrogen Abstraction Processes to Chemical and Electrochemical Conversion Processes*

*D.G. Whitten* **$105,000**
*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". A major area of emphasis is on photochemical redox reactions initiated by electron transfer quenching of an excited state that can be followed by a variety of subsequent events (e.g., proton transfer, hydrogen atom abstraction processes, and carbon–carbon bond cleavage). We are also investigating other possible sequences for photoredox reactions, mostly involving dyes or other chromophores that absorb light in the visible or near-ultraviolet regions. Studies of reactivity of molecules entrapped within inclusion complexes or solubilized specifically at an interface are also made. These studies have already shown that in several cases novel photochemical reactivity can be associated with these specific microenvironments, and present work seeks to establish the systematic relationship between the two for a number of different reactive systems.

## Stanford University
## Stanford, California 94305

### *189. Energy Transfer Processes in Solar Energy Conversion*

*M.D. Fayer* **$117,200**
*Department of Chemistry*

This project examines energy transport processes in nontraditional systems using picosecond and other optical techniques and statistical mechanical theoretical methods. A wide variety of situations in both natural and man-made systems cannot be modeled as periodic arrays of molecules. In many systems, inherent disorder and characteristic size and shape play key roles in determining energy dynamics. We have developed the first accurate and detailed statistical mechanics theory of energy transport in disordered systems with finite volume. We are using a picosecond transient holographic grating technique and picosecond fluorescence mixing methods with conventional fluorescence and absorption experiments. We have developed a general theoretical approach to describe energy transport in any geometrical arrangement of molecules, and applied this to two-dimensional and anisotropic three-dimensional systems. In particular we have performed calculations for monolayers, bilayers, multilayers, and polymer coils, with fundamental energy transport processes related to experimental observables. Experiments on energy transport among molecules attached to a polymer backbone show quantitative agreement with theory. We have also examined the effects of angular fluctuations on electron transfer in donor–acceptor pairs. Using picosecond holographic grating methods, we have obtained the first direct measurements of ground-state electron transfer between a negative and a positive ion. The study of electron transfer, initiated by optical excitation, between donors and acceptors in excited states and ground states on ultrafast time scales reveals the dynamical details important in natural and laboratory chemical electron transfer reactions.

### *190. Fundamental Electron Transfer Processes at the Semiconductor–Liquid Interface*

*N.S. Lewis* **$80,000**
*Department of Chemistry*

Fundamental electron transfer properties at semiconductor–liquid junctions have been studied as a function of systematic changes in bulk semiconductor composition and in other external parameters. From plots of the open-circuit voltage vs. temperature, we observe the activation energy for the dominant recombination mechanism for n-GaAs and n-$Al_{1-x}Ga_xAs$ anodes in contact with $C_2H_5CN$–ferrocene$^{+/0}$ electrolyte to be equal to the bandgap for all compositions. Open-circuit voltages of 0.81 to 0.82 V have been measured for n-GaAs/$CH_3CN$–$FeCp_2{}^{+/0}$ solar cells at 88.0 mW/cm$^2$ tungsten-halogen irradiation. From our kinetic data, we conclude that the n-GaAs/$CH_3CN$–$FeCp_2{}^{+/0}$ interface is controlled by recombination in surface traps. Excellent spectral response characteristics have also been measured for n-$Al_{1-x}Ga_xAs$/$CH_3CN$–$FeCp_2{}^{+/0}$ systems. Spectral response characteristics and photocurrents of mirror-finished n-GaAs with moderate minority carrier diffusion lengths in aqueous KOH–$Se^{2-}$–$Se_2{}^{2-}$ have been shown to improve with matte etching, which is ascribed to an increased effective minority carrier collection length induced by the matte topology. Kinetic and thermodynamic parameters of the n-$Al_{1-x}Ga_xAs$ and n-$GaAs_{1-x}P_x$ systems in $CH_3CN$ and in aqueous selenide are currently being studied.

## Syracuse University
## Syracuse, New York 13244

### *191. Photochemical Solar Energy Conversion Utilizing Semiconductors Localized in Membrane Mimetic Systems*

*J.H. Fendler* **$85,000**
*Department of Chemistry*

The project objective is the development of surfactant vesicles, polymerized surfactant vesicles, and bilayer lipid membranes (BLMs) as media for organizing components of the artificial photosyntheic apparatus. Emphasis is on the use of surfactant aggregate-stabilized catalyst-coated colloidal semiconductors as sensitizers and relays. Our approach includes steady-state and nanosecond time-resolved absorption and emission spectroscopy, photolysis, and the determination of quantum yields for hydrogen production in sacrificial water reduction systems. Efficient charge separations are obtained on using surfactant vesicle-stabilized rhodium-coated colloidal CdS as sensitizers and benzyl alcohol as a sacrificial electron donor. Optimizations are conducted by finely tuning the morphology of CdS particles and by using mixed *in situ* generated vesicle-stabilized CdS–ZnS colloids. Methods for the preparation and characterization of BLM-stabilized colloidal semiconductors are being developed.

## University of Tennessee
**Knoxville, Tennessee 37996**

### *192. Studies of Radiation-Produced Radicals and Radical Ions*

*T.F. Williams* **$106,000**
*Department of Chemistry*

The basic objective of this project is to characterize the structure and reactivity of important free radical and radical ion intermediates generated by irradiation of molecular systems. Radical cations are generated under matrix-isolation conditions by $\gamma$-irradiation of solid solutions of the parent compounds 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. Electron spin resonance spectroscopy is used to characterize these paramagnetic species. Specific projects include studies of (1) spin delocalization in fluorocarbon and fluorine-containing radical anions, (2) radical cation–Freon solvent $\sigma^*$ complexes, (3) radical cation rearrangements involving ring opening (oxirane cation) or hydrogen atom transfer (trimethyl phosphate cation), (4) long-range hyperfine interactions in radical cations of carbonyl compounds, and (5) ligand structure of organometallic cations derived from Group IVB organometals. Additional work is in progress on the photogeneration of radical ions in colloidal titanium dioxide solutions.

## University of Texas
**Austin, Texas 78712**

### *193. Organic Redox Phototransformations at Chemically Modified Surfaces*

*M.A. Fox* **$81,600**
*Department of Chemistry*

Exploratory and mechanistic studies of new chemical transformations of organic molecules at native and chemically modified surfaces represent the goal of this research. New electrode materials are prepared by adsorption, covalent attachment, polymerization, and mulling with electroactive or light-sensitive materials, and physical studies of the properties of these materials are conducted. Both photocatalytic and photosynthetic organic reactions can be initiated by electron exchange induced by visible-light excitation of either native or chemically modified semiconductor surfaces. Mechanisms for charge migration through polymer layers coating electrodes are being determined. Photophysical characterization of dye-excited states as a function of their microenvironment are being obtained. New metal nonoxides and p-type semiconductors are also investigated, and the search for new reactions on these novel materials is continuing.

### *194. Photoinduced Charge Separation by Polymer-Bound Chromophores*

*S.E. Webber* **$115,000**
*Department of Chemistry* **(18 mo.)**
*M.A.J. Rodgers*
*Center for Fast Kinetics Research*

This project involves study of water-soluble polymer molecules to which chromophores are covalently attached. In many cases these systems are amphiphilic in that the polymer backbone is largely water soluble while the pendant chromophores may be hydrophobic. The chemical fate of the photoexcited residue is controlled by changing the nature of the polymer backbone and/or the environmental conditions. We are particularly concerned with electron or hole transfer to an oxidizable or reducible substrate present in the surrounding medium, and subsequent separation of the radical pairs. This is the fundamental step for conversion of photon energy to chemical energy. In addition we are studying such systems as possible models for photon harvesting systems in which several different chromophores can absorb a broad range of the solar spectrum, eventually channeling the absorbed energy to a chemically reactive center. Another aspect of this work is the study of photoinduced ionization in these polymeric systems.

## Washington University
**St. Louis, Missouri 63130**

### *195. Reaction Studies of Hot Silicon, Germanium, and Carbon Atoms*

*P.P. Gaspar* **$85,000**
*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 at high energies by nuclear transformations such as $^{31}P(n,p)^{31}Si$, $^{76}Ge(n,2n)^{75}Ge$, and $^{12}C(p,pn)^{11}C$, and at low energies by thermal evaporation. Reactive intermediates such as $SiH_2$ and $SiMe_2$ are generated by pyrolysis and photolysis. Extrusion of dimethylsilylene from 1,1-dimethyl-1-silacyclopent-3-enes has been found to be an efficient process. *Cis*-2-alkyl-3-alkenyl-1-silacyclopropanes have been shown to undergo concerted rearrangement by a retro-ene reaction yielding bis-alkenylsilanes. Trimethylsilylsilylene has been shown to rearrage via a methyl-shift to trimethyldisilene, which in turn rearranges via a hydrogen shift, completing a novel transposition process. Absolute rate measurements on silylene reactions by laser flash photolysis provide important new mechanistic insights.

## Wayne State University
**Detroit, Michigan 48202**

### *196. Dynamics of Charge-Transfer Excited States Relevant to Photochemical Energy Conversion*

*E.C. Lim* **$80,000**
*Department of Chemistry*

This research addresses basic questions concerning the energetics and dynamics of charge-transfer (CT) excited states that are relevant to photochemical energy conversion. We study CT excited states of electron donor–acceptor (EDA) complexes and transition metal complexes in gas phase and in condensed phase, using laser-based techniques (fluorescence, multiphoton ionization, and so forth). A systematic study of the photophysical properties of EDA complexes containing alkyl benzenes as electron donors reveals that charge recombination is less efficient for $D_2A$ (of sequence DDA) than for DA. Deuteration of methyl hydrogens has relatively large effects on the nonradiative decay rate ($k_{nr}$) of DA, but only minor effects of $k_{nr}$ of $D_2A$. The effect of ring deuteration is larger for $D_2A$ than for DA.

with the neutral beam are shown to be well accounted for by a model involving electron-stimulated desorption of alkali atoms. A simple model is proposed for the compensation observed for changes of the preexponential factor and activation energy in rate coefficients for the desorption of molecules from surfaces undergoing surface phase transitions. The isomerization of perfluoroDewarbenzene to perfluorobenzene can be produced in yields of 10% after single energetic collisions with a surface of polytetrafluoroethylene. The yield of ions produced when a beam of sodium atoms strikes a Si(111) surface is increased over the equilibrium value observed for thermal beams by a factor of 10 or more when the kinetic energy of the incoming atoms is increased to 14 eV. The yield is sensitive to the dynamics of electron exchange between the surface and the ion.

## University of California
## Davis, California 95616

### *201. Laser Studies of the Dynamics of Atom–Molecule Reactions*

*W.M. Jackson* **$57,000**
*Department of Chemistry*

A tunable dye laser is used with a low-power pulsed ArF laser to measure the rate constant for the reaction of CN radicals with saturated and unsaturated hydrocarbons. These rate constants can be determined as a function of the vibrational energy of the CN radicals. The room-temperature rate constants for CN reactions with the saturated hydrocarbons from $CH_4$ to $C_7H_{16}$ have been determined and found to increase from $5.6 \times 10^{-13}$ to $2.3 \times 10^{-10}$ $cm^3s^{-1}$. This large increase in the rate constants has been explained by invoking an attractive potential to increase the overall collisional rate. This attractive potential leads to a long-lived complex that promotes intramolecular energy transfer. The larger the amount of intramolecular energy transfer in the complex, the higher the probability for the formation of stable products. This model would predict that the rate constant should exhibit a negative activation energy, and experiments are in progress to determine if this is the case.

## University of California
## Irvine, California 92717

### *202. Laser Studies on Internal State Dependence of Excitation and Deexcitation Processes*

*E.K.C. Lee* **$110,000**
*Department of Chemistry* **(18 mo.)**

This research project is designed to measure the state-to-state rates of excitation and deexcitation of small polyatomic molecules in single rotational and vibrational levels of the excited electronic state. Emphasis will be placed on studies of small free radicals and intermediate molecules important to combustion and flame chemistry. The experimental techniques of laser-induced fluorescence spectroscopy and laser-induced photofragment luminescence spectroscopy by one-photon and two-photon absorption will be studied in frequency-domain and time-domain. A search for new electronic states as well as new fluorescence and chemiluminescence channels will be made. Variations in the quantum yields of fluorescence, radiative lifetimes, molecular perturbations that affect radiative processes, collisional energy transfer rates, and temperature dependence as a function of rotational and vibrational states are being studied with molecules such as HCO.

## California Institute of Technology
## Pasadena, California 91125

### *203. Studies in Spectroscopy and Chemical Dynamics*

*A. Kuppermann* **$98,000**
*Chemistry and Chemical Engineering Division*

Free radicals containing carbon, hydrogen, nitrogen, or oxygen are of major importance for combustion processes. Many such radicals have low-lying electronic states that may be energetically accessible at temperatures that occur under combustion conditions. We are using the technique of low-energy-variable angle electron impact spectroscopy to study these electronic states. An investigation of $CH_3$ has been recently completed. Many of the elementary reactions of interest to combustion involve free radicals. We are performing two-color laser experiments in which a free radical is produced by pulsed ultraviolet laser, and the nascent product of its reaction with another molecule is detected by laser-induced-fluorescence produced by a time-delayed vacuum-ultraviolet laser pulse. In the initial experiments, hydrogen atoms are the reagent and HD molecules the detected product. The objective is to obtain information about the translational energy dependence of the cross section of such reactions and its relation to activation energies.

## Catholic University of America
## Washington, District of Columbia 20064

### *204. Kinetics and Mechanisms of Key Elementary Processes of Importance to High-Temperature Combustion Chemistry*

*M.C. Lin, W.A. Sanders* **$69,400**
*Department of Chemistry*

A systematic, multithrust study of the kinetics and mechanisms of key elementary chemical processes relevant to high-temperature combustion chemistry is being conducted. The project combines state-of-the-art experimental work with computer modeling and theoretical interpretation of observed kinetic data. The major effort is concentrated in three areas: (1) shock-tube studies of high-temperature elementary reactions involved in the combustion of benzene and related chemical processes; (2) two-laser pump-probe measurements of high-temperature free-radical reaction kinetics, with particular emphasis on processes leading to $NO_x$ formation; and (3) interpretation and extrapolation of low-temperature rate constants for reactions involving long-lived intermediates by means of the RRKM theory.

## University of Colorado
## Boulder, Colorado 80309

### *205. Laser Photoelectron Spectroscopy of Ions*

*G.B. Ellison* **$95,000**
*Department of Chemistry*

We are studying the spectroscopy of chemically reactive intermediates in combustion. We prepare mass-selected negative ion beams ($M^-$) and irradiate them with an intracavity, CW Ar II laser operating on a single line ($\lambda_0$ = 488 nm). Following with the neutral beam are shown to be well accounted for by a model involving electron-stimulated desorption of alkali atoms. A simple model is proposed for the compensation observed for changes of the preexponential factor and activation energy in rate coefficients for the desorption of molecules from surfaces undergoing surface phase transitions. The isomerization of perfluoroDewarbenzene to perfluorobenzene can be produced in yields of 10% after single energetic collisions with a surface of polytetrafluoroethylene. The yield of ions produced when a beam of sodium atoms strikes a Si(111) surface is increased over the equilibrium value observed for thermal beams by a factor of 10 or more when the kinetic energy of the incoming atoms is increased to 14 eV. The yield is sensitive to the dynamics of electron exchange between the surface and the ion.

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## University of Colorado
## Boulder, Colorado 80309

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*Department of Chemistry*

We are studying the spectroscopy of chemically reactive intermediates in combustion. We prepare mass-selected negative ion beams ($M^-$) and irradiate them with an intracavity, CW Ar II laser operating on a single line ($\lambda_0$ = 488 nm). Following detachment of the ions, we energy analyze the scattered electrons. From an analysis of the resulting photoelectron spectrum, we can deduce the electron affinity of the neutral (M) and the heats of formation of M and $M^-$. We can also extract the molecular geometries of the negative ion and the final neutral. We have completed a study of the related ions, $SO_2^-$, $S_3^-$, and $S_2O^-$. Our analysis suggests that the $SO_2^-$ ion has a bond length of r(S-O) = 1.523 ± 0.020 A and a bond angle $\alpha_{OSO} = 115.6° \pm 2°$. The photoelectron spectra yield the following electron affinities and heats of formation: $EA(SO_2) = 1.107 \pm 0.008$ eV, $EA(S_3) = 2.093 \pm 0.025$ eV, $EA(S_2O) = 1.877 \pm 0.008$ eV; $\Delta H_{f298}(SO_2^-) = -98.0 \pm 0.2$ kcal/mol, $\Delta H_{f298}(S_3^-) = -18.0 \pm 0.6$ kcal/mol, $\Delta H_{f298}(S_2O^-) = -57.5 \pm 0.3$ kcal/mol. We have recently examined the photoelectron spectra of $SiH_3^-$ and $SiD_3^-$. We find the following electron affinites: $EA(SiH_3) = 1.406 \pm 0.014$ eV, $EA(SiD_3) = 1.386 \pm 0.022$ eV. From an analysis of the peak splittings and intensities, we extract potential energy curves for the umbrella mode of the $SiH_3^-$ negative ion and the $SiH_3$ radical. Both species are pyramidal molecules with inversion barriers of 9,000 ± 2,000 $cm^{-1}$ for $SiH_3^-$ and 1,900 ± 300 $cm^{-1}$ for $SiH_3$. The bond angle α(H–Si–H) for $SiH_3^-$ is 94.5° while the value for the radical, $SiH_3$, is 112.5°.

### *206. Time-Resolved Studies of Free Radicals and Laser-Initiated Chain Reactions*

*S.R. Leone* **$80,000**

*Department of Chemistry and Biochemistry*

Time and wavelength-resolved infrared emission techniques are used to study free radical production and reactions. Infrared emission spectra have been obtained and analyzed for combusting mixtures of low-pressure chlorine with hydrocarbons. A method has been developed to measure the absolute rate coefficients of methyl radical reactions with molecules such as chlorine, bromine, and hydrogen iodide. Intramolecular vibrational relaxation processes have been observed in the ground electronic state of hydrocarbons by exciting the first CH overtones and detecting the reduction in emission from these states. Laser multiphoton ionization has been used to detect the state distributions of molecular nitrogen. Laser photodissociation of acetone has provided fragment infrared emission spectra of the dissociation products and rates of vibrational deactivation of methyl radicals.

## Columbia University
## New York, New York 10027

### *207. Energy Partitioning in Elementary Gas-Phase Reactions*

*R. Bersohn* **$86,000**

*Department of Chemistry*

Elementary atom–molecule reactions are studied by laser-induced fluorescence and spectroscopic techniques for detection of atoms are developed. Hydrogen (H) atoms are detected immediately after their production by chemical reactions or photodissociation. Use of a narrow-band laser permits the determination of the Doppler broadened line shape of the 1s → 2p absorption that yields the velocity distribution. High-speed (30 km/s) H atoms are generated by photodissociation in the midst of a rare gas. The velocity distribution is observed to evolve from an initial sharp, almost delta, function through a warm Boltzmann, and eventually to a room-temperature Boltzmann distribution. This relaxation process, analogous to the moderation of a fast neutron, has never been observed in such detail. H atoms are generated from toluene and related molecules into which fixed amounts of energy have been pumped. The rate of formation of the H atoms ($5 \times 10^6 s^{-1}$) and their velocity distributions are being studied as tests of unimolecular reaction rate theory. Both measurements indicate that when the molecule has an internal energy E and requires $E_0$ in a particular bond to dissociate, the remaining energy $E-E_0$ is not distributed statistically over all the molecular vibrations.

## Cornell University
## Ithaca, New York 14853

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

*T.A. Cool* **$88,000**

*Department of Applied and Engineering Physics*

A laser-based technique is proposed, to provide nonintrusive density measurements of the $C_2H$ radical for studies of the chemistry of precursors to soot formation in hydrocarbon flames. The approach is based on the resonance-enhanced multiple-photon ionization (REMPI) of $C_2H$, a method that has been successfully used for the detection of other combustion species, including O, C, H, NO, PO, CO, $C_2O$, CH, and $CH_3$. The development of such a technique for the detection of $C_2H$ would be valuable since the more conventional methods of vacuum ultraviolet spectroscopy and laser-induced fluorescence have not succeeded for $C_2H$ detection to date. Two stages of research are proposed. In the first, mass spectrometric detection of $C_2H^+$ REMPI ions will be used to identify high-lying Rydberg states of $C_2H$ by REMPI ion spectroscopy. A quadrupole mass spectrometer will be used to detect photolytically produced $C_2H$. In the second stage, calibration procedures will be established to permit absolute density measurements of $C_2H$ to be made in flow reactors, flash photolysis experiments, and hydrocarbon flames with REMPI electron detection methods. The effort is designed to provide fundamental spectroscopic data on the elusive ethynyl radical and to permit a better understanding of its role in the complex chemistry of soot formation in hydrocarbon flames.

## Emory University
## Atlanta, Georgia 30322

### *209. Theoretical Studies of Combustion Dynamics*

*J.M. Bowman* **$67,000**

*Department of Chemistry*

The objective of our current research is to establish a quantum mechanical theory of recombination reactions and to apply it to a study of the H + CO → HCO reaction, an important process in hydrocarbon combustion. We have achieved the first objective by generalizing a theory of atom–atom recombination due to Smith. The key quantity is the time delay due to the collison. The calculation of this quantity for the H + CO system is proceeding with large-scale coupled channel scattering calculations being performed on the MFE CRAY-XMP supercomputer. An accurate *ab initio* potential, due to Harding, is being used in these calculations. Thus far we have obtained the time delays over a wide range of energies for the simplest case of zero total angular momentum and treating CO as rigid rotor.

Though this is the simplest case, it provides very important benchmark calculations against which various approximate theories can be tested. In particular we intend to test the RRKM theory immediately after our calculations are complete. When complete, these calculations will provide the most accurate predictions of the rate of recombination of H with CO.

## Howard University
## Washington, District of Columbia 20059

### *210. Photolytic Processes for Measurement of Combustion Heats of Formation and Reaction Rates*

*J. Halpern, H. Okabe* **$55,000**
*Department of Chemistry*

Laser photolysis is an efficient and sudden source of free radicals in the gas phase. This study includes (1) combining laser photolysis with flash absorption spectroscopy and ESR detection to measure the kinetics of polyatomic radicals and triplets to study the reaction kinetics of acetylenic systems; and (2) using tunable vacuum ultraviolet light generated in a discharge lamp-monochromator system, or by frequency shifting of an intense laser source to measure the heat of formation of RO radicals (R = $CH_3$, $C_2H_5$, and t-$C_4H_9$). These radicals are important intermediates in combustion and low-temperature oxidation of hydrocarbons.

## University of Illinois
## Chicago, Illinois 60680

### *211. Kinetics of Elementary Atom and Radical Reactions*

*R.J. Gordon* **$100,000**
*Department of Chemistry*

The objectives of this research are to measure the reaction rates and to study the dynamics of elementary gas phase reactions. One system being studied is the reaction of ground-state oxygen atoms with $H_2$, $D_2$, and HD. Flash photolysis with resonance fluorescence detection of oxygen atoms has been used to measure the rate constants of these reactions between 325 and 475 K. The branching ratio for O + HD has been determined by using laser-induced fluorescence to measure the relative concentrations of OH and OD products. In a second study the relaxation of highly excited molecules has been investigated using a $CO_2$ laser to excite a donor molecule while detecting infrared fluorescence from an acceptor molecule. For $SF_6$ + $N_2O$ we measured the rate of vibrational energy transfer to $N_2O$ as a function of $SF_6$ energy. We have found that the bending mode of $N_2O$ is preferentially excited and that it relaxes an order of magnitude more slowly than the asymmetric stretching mode. In a third study we have investigated the production of electronically excited NH radicals generated by photolyzing HNCO. We have discovered that excited triplet NH is produced in the presence of $O_2$. The mechanism for this phenomenon, which involves metastable $O_2$ and NH states, is being investigated.

### *212. Shock Tube Studies of High-Temperature Hydrocarbon Pyrolysis Rates*

*J.H. Kiefer* **$80,000**
*Department of Chemical Engineering*

The purpose of this project is to determine rates and mechanism for fuel hydrocarbon pyrolysis at high temperatures. The measurements are made in the shock tube (providing arbitrary, precise, and externally set temperatures) with two very high resolution laser diagnostic techniques. These two are laser schlieren measurement of density gradient (net endothermic rate) and the new method of excimer laser flash absorption, which provides absorption profiles in the ultraviolet with ~ 0.03 microsecond resolution. Previous work has defined much of the pyrolysis kinetics of propane, propene, ethane, ethylene, benzene, and 1,3-butadiene. Recent measurements have given a mechanism and rate for ethylbenzene decomposition and a partial understanding of toluene pyrolysis. Flash absorption measurements at 220 nm have now confirmed the rate and mechanism for 1,3-butadiene dissociation derived from the laser schlieren data. Recent laser schlieren work has been the study of cyclohexene dissociation to 2000 K, and a new study of vinyl acetylene pyrolysis. Flash absorption measurements have also been obtained for the cyclohexene dissociation.

## Illinois Institute of Technology
## Chicago, Illinois 60616

### *213. Studies of Combustion Kinetics and Mechanisms*

*D. Gutman* **$120,000**
*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 multiple-photon-induced decomposition of suitable precursors by a $CO_2$ TEA laser or by direct ultraviolet laser photolysis. Ensuing reactions are monitored using a photoionization mass spectrometer capable of recording the time evolution of either reactants or products. Reactions of hydrocarbon free radicals with molecular oxygen are being investigated as a function of pressure and temperature to establish their mechanisms, to measure their rate constants, and to determine important thermochemical parameters. Studies of the $C_2H_5 + O_2$ and $C_3H_7 + O_2$ reactions are revealing important mechanism changes near 700 K that are responsible for important changes in the stable products produced during combustion around this temperature. The equilibria between hydrocarbon free radicals (including $CH_3$, $C_2H_5$, $C_3H_5$, and $C_3H_7$) with molecular oxygen are being studied between 600 and 700 K to directly measure the enthalpy change of these important combustion reactions. This information is now being used in combustion models that predict flame properties and product distributions.

## University of Kentucky
## Lexington, Kentucky 40506

### 214. *Laser Spectroscopy and Dynamics of Combustion Intermediates*

*D.J. Clouthier* **$87,500**
*Department of Chemistry*

Experiments are in progress to study the vibrational and electronic spectra and excited-state dynamics of a variety of sulfur species that are analogs of important oxygen-containing combustion intermediates. Results will provide the necessary data for future laser-based measurements of the intermediacy of these sulfur species in the oxidation and pyrolytic degradation of larger organic sulfur compounds in fuels. Specific molecules chosen for study are disulfur monoxide ($S_2O$), thioformaldehyde ($H_2CS$), thioketene ($H_2CCS$), and the free radicals HCCS, HCS, and $C_2S$. Experimental techniques will include Fourier transform interferometry, laser and supersonic jet spectroscopy, and emission lifetime and quantum yield measurements.

## Massachusetts Institute of Technology
## Cambridge, Massachusetts 02139

### 215. *Aromatics Oxidation and Soot Formation in Flames*

*J.B. Howard* **$87,000**
*Department of Chemical Engineering*

The objective of this research is to provide basic information on the kinetics and mechanisms of aromatics oxidation and soot formation in flames. The research is based on detailed measurements of profiles of soot particle number concentration, particle size distribution, and stable and radical gas species concentrations through the reaction zone of low-pressure flat premixed flames. A molecular-beam sampling instrument with on-line mass spectrometry is used for gas species measurement. Soot particles are studied by laser scattering and adsorption measurements in the flame and analysis of beam deposits. Net reaction rates calculated from these measurements will be used in screening tests of hypothetical reaction mechanisms. The gas species profiles are used to test and to extend existing flame chemistry models. The work is expected to lead to an improved understanding of the chemistry of soot formation and aromatics reactions in flames. Calculations using previous data indicate that aromatics in the presence of oxidizing species in flames are consumed more rapidly than in the nonoxidizing conditions of pyrolysis experiments.

### 216. *Depopulation Rates for Combustion-Related Species in Long-Lived (>100μs) Vibrationally or Electronically Excited Levels*

*J.L. Kinsey, R.W. Field* **$125,000**
*Department of Chemistry*

In this project, a new technique, stimulated emission pumping, is being used to study individual levels of polyatomic molecules with chemically significant amounts (up to ~3.5 eV) of vibrational excitation. Current effort focuses on the acetylene molecule, HCCH, in its electronic ground state ($X^1\Sigma g$). Collections of individual rotation-vibration levels as much as 28,000 $cm^{-1}$ above the vibrationless level have been analyzed to obtain information about the transition from regular to ergodic behavior in a molecular system. New statistical methods relying on Fourier-transformed spectra have been used on high-resolution (~0.03 $cm^{-1}$) and low-resolution (~0.5 $cm^{-1}$) data in the 28,000 $cm^{-1}$ region to obtain information on intermolecular energy randomization on widely different time scales. These studies are being extended to levels at 14,000 to 16,000 $cm^{-1}$ to look for evidence of the vinylidene radical ($H_2CC$). Parallel investigations probe triplet levels of acetylene at ~45,000 $cm^{-1}$, using Zeeman quantum beat spectroscopy and anticrossing spectroscopy. These reveal details of nonadiabatic coupling of triplets to singlet levels of both the $\tilde{X}$ and $\tilde{A}$ electronic states, and the densities of vibrational levels in this energy range.

## University of Michigan
## Ann Arbor, Michigan 48109

### 217. *Energy Transfer Properties and Mechanisms*

*J.R. Barker* **$80,000**
*Department of Atmospheric and Oceanic Science*

This project studies the mechanisms and properties of energy transfer involving moderate-sized molecules. In part, focus is on resolving current controversies about the temperature dependence and energy dependence of the average energy transfer step-size in deactivating collisions. Time- and wavelength-resolved infrared fluorescence is used to monitor the level of vibrational energy in excited molecules prepared by pulsed laser excitation. Improvements include (1) tunable ultraviolet laser excitation and tunable excitation in the visible, (2) new calibration methods designed to reduce experimental uncertainties and extend the energy range of the experiments, and (3) investigation of several molecules that have been studied by time-resolved ultraviolet absorption. Experiments are underway to investigate the mechanisms of energy transfer. The products of energy transfer are investigated by monitoring their infrared fluorescence, and laser-induced fluorescence is used to assess the importance of vibrational levels produced in the energy-transfer process. Isotopically substituted isomers are used to investigate the effects of dipole moment, symmetry properties, fundamental vibrational frequencies, and so forth. Collisional/reaction master equation calculations indicate whether steady state is attained in high-temperature systems and whether unimolecular rate theory must be modified to account for the non-steady-state conditions that may occur in hostile environments.

## University of Minnesota
## Minneapolis, Minnesota 55455

### 218. *State-to-State Dynamics of Molecular Energy Transfer*

*W.R. Gentry, C.F. Giese* **$92,000**
*Departments of Chemistry and Physics*

The project objective is to learn about the microscopic dynamics of molecular energy transfer by studying individual molecular collisions at a state-resolved level of detail. A novel apparatus has been constructed for this work, in which molecular beams of the selected molecules are crossed at a variable intersection angle, and the collision products are detected state-selectively by laser-induced fluorescence. Our first experiments were concerned with vibrational excitation of diatomic and polyatomic molecules. During the last year, the addition of a new laser offering much higher spectroscopic resolution has permitted us to observe the details of the rotational excitation that occurs alone or in combination with vibrational excitation. The kinetic energy dependence of large-J rotational excitation in $I_2$ + He collisions exhibits structure that is directly sensitive to the angle dependence of the interaction potential.

219. ***Variational Transition State Theory***
*D.G. Truhlar* **$77,000**
*Department of Chemistry*

This project is concerned with the application of variational transition state theory and semiclassical tunneling calculations to gas-phase reactions and processes at surfaces. Recent progress includes: (1) applications to atom–diatom processes using global or semiglobal analytic representations of potential energy surfaces; (2) applications to polyatomic systems (i.e., systems with four or more atoms) using global or semiglobal analytic representations of potential energy surfaces; and (3) development of new methods for combining *ab initio* electron structure calculations of reaction-path potentials with variational transition state theory and reaction-path tunneling calculations.

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

220. ***Laser Studies of Chemical Dynamics at the Gas–Solid Interface***
*R.R. Cavanagh, D.S. King* **$70,300**
*Center for Chemical Physics*

Experimental measurements of the internal state distributions of molecules desorbed from metal surfaces in ultrahigh vacuum are made to understand energy transfer at metal surfaces at a microscopic level. Molecules are desorbed by resistive heating or by nonresonant laser heating and probed by laser-excited fluorescence. The dynamics manifest upon interaction with a variety of metals and under the presence of coadsorbates such as CO or $NH_3$ have been examined. In all cases the rotational state distributions have been found to be Boltzmann in character, but not necessarily described by a temperature equal to the surface temperature during desorption; the degree of rotational accommodation reflecting the dynamics of the final chemical bond-breaking step. In the laser-heating experiments on platinum foils, optically detected time-of-flight measurements clearly show the presence of non-Boltzmann velocity distributions for the molecules desorbed. There is no universal relationship between the rotational, vibrational, or kinetic energies of these desorbing species.

221. ***Kinetics Data Base for Combustion Modeling***
*J.T. Herron* **$100,000**
*Center for Chemical Physics*

The project objective is to compile, evaluate, and publish data on rate constants of elementary chemical reactions relevant to a detailed description of the combustion of hydrocarbons. All possible reactions will be considered. Evaluation involves critical examination of experimental data, comparison with data on analogous reactions, and the use of modern chemical kinetic theory to provide a framework for the evaluation. Results are presented in the form of individual data sheets that can be periodically upgraded as new data become available. The approach is to start with the simplest systems and work up to more complex ones. Evaluation is now complete on systems containing the light saturated hydrocarbons. Future work will involve continued upgrading of this data and expansion to include data on unsaturated hydrocarbons, and sulfur-, nitrogen-, and oxygen-containing organic species.

## University of New Orleans
## New Orleans, Louisiana 70148

222. ***Identification and Temporal Behavior of Radical Intermediates Formed During the Combustion and Pyrolysis of Gaseous Fuels***
*R.D. Kern, Jr.* **$63,000**
*Department of Chemistry*

High-temperature studies of the gas-phase pyrolyses of benzene, toluene, ethylbenzene, butadiene, allene, and acetylene have revealed information pertaining to the mechanisms attendant to aromatic ring rupture and ring formation. The concentration profiles for these decompositions are obtained by analyzing reflected shock zone gas with time-of-flight (TOF) mass spectrometry. By combining the TOF results with data produced by other workers using laser schlieren densitometry and atomic resonance absorption, mechanisms have been constructed that model the experimental profiles successfully. Some important findings include: (1) low concentrations of phenyl radical observed in $C_6H_6$ pyrolysis; (2) evidence that the primary step in $C_7H_8$ decay at high temperatures is $C_6H_5 + CH_3$ instead of $C_7H_7 + H$ and the contributions of reverse and secondary reactions; (3) the favored channel is $C_7H_7 + CH_3$ compared to $C_8H_9 + H$ in $C_8H_{10}$ decomposition; (4) the increased amount of $C_6H_6$ formed during $C_3H_4$ thermolysis as contrasted to that formed from an equivalent amount of 1,3-$C_4H_6$; and (5) the role of $C_3H_3$ in $C_6H_6$ formation as demonstrated in the decomposition of 1,2-$C_4H_6$. These facts are most helpful in understanding the problem of soot formation from aromatic fuels.

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

223. ***Multiphoton Interactions in Molecules with Picosecond Laser Pulses***
*H.-S. Kwok* **$68,500**
*Department of Electrical and Computer Engineering*

High-power picosecond laser pulses are employed in this project to study the multiphoton absorption and dissociation behavior of simple polyatomic molecules. Tunable 20 to 200 ps $CO_2$ and dye laser pulses are used individually or in a pump-probe arrangement to measure the excitation characteristics of vibrationally hot molecules. Intramolecular and intermolecular energy transfer rates are studied in the collisional and collisionless regimes. Information on the vibrationally hot molecules in the quasi-continuum is of vital importance in the understanding of gas-phase reaction dynamics. During the past year, it was found that the multiphoton absorption spectra in $SF_6$, $C_2F_5Cl$, and $C_3F_7I$ were inhomogeneously broadened. Intramolecular energy transfer did not seem to contribute to any line broadening. It was also discovered that the absorption cross section increased significantly and the line width decreased as the $CO_2$ laser pulse duration was decreased. These observations were consistent with a coherent multi-tier interaction picture. The dynamics of the energy coupling with the QC can be studied by this technique. Picosecond ultraviolet-infrared double resonance experiments are planned for the coming year.

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

### 224. *Multiphoton Ionization Spectroscopy and Photochemistry of Transient Species*
*P.M. Johnson* **$73,200**
*Department of Chemistry*

This project is primarily concerned with the development of new methods of acquiring the multiphoton spectra of transient species such as triplet metastables and radicals. These species are generated in ways related to combustion processes so that insight may also be gained into the production mechanisms. In one method, radicals and triplets are generated by a pulsed electric discharge at the orifice of a pulsed supersonic valve, providing cooling in the expansion and a rapid transition into a collisionless condition. This technique has proven to be a bountiful source of triplet and radical species whose multiphoton spectra have never been explored. It should also be possible to create discharge-initiated reactions between two species in the expansion. Reaction intermediates will be rapidly isolated by the expansion and can be studied by multiphoton ionization mass spectrometry. To date, we have successfully studied the triplet states of argon, carbon monoxide, and nitrogen as well as the radical CCl. By using this technique, we have been able to precisely determine the energy of the lowest triplet state of benzene, and determine the energies of many previously unmeasured states of the nitrogen molecule.

## University of Pennsylvania
### Philadelphia, Pennsylvania 19104

### 225. *Dynamics of Vibrationally Exicted Polyatomic Molecules and Their Unstable Isomers on the Electronic Ground State Potential Surface*
*H.-L. Dai* **$81,000**
*Department of Chemistry* **(9 mo.)**

This project will generate crucial information for the understanding and design of chemical reactions of highly vibrationally excited molecules. Experiments will reveal the fine details of structure and dynamics on the electronic ground state for many molecules important in the chemistry of energy production. The highly vibrationally excited molecules will be studied through the combination of a selective excitation method, stimulated emission pumping (SEP), and subsequent detection of infrared fluorescence with frequency resolution. The SEP scheme driven by two laser pulses will prepare molecules in single vibrational eigenstates with as much as 80 kcal/mole energy. The fluorescence spectra will be used to characterize the wave function of the high vibrational eigenstates and to examine the extent of intramolecular relaxation as a function of vibrational energy and motion. Small molecules such as $SO_2$, HCP, $C_2H_2$, and $H_2CO$, and larger molecules such as alkyl aromatic compounds will be studied. At relatively high energies the eigenstate wave function will spread over to structural isomers that exist on the potential surface. Spectral features in the infrared fluorescence may originate from all of the energetically accessible isomers. Thus the dispersed infrared fluorescence can be used to identify the existence of the isomers, particularly the extremely unstable and transient ones. These diagnostics will be first applied to the $SO_2$ molecule with an SOO isomer and a ring isomer, as well as on the acetylene–vinylidene system.

## Princeton University
### Princeton, New Jersey 08544

### 226. *Comprehensive Mechanisms for Combustion Chemistry: An Experimental and Numerical Study with Emphasis on Applied Sensitivity Analysis*
*F.L. Dryer* **$95,100**
*Department of Mechanical and Aerospace Engineering*

This project is an integrated effort to determine the reaction mechanisms responsible for oxidation of hydrocarbon and alcohol molecular structures under conditions representative of combustion environments. Such mechanisms are useful to focus on areas where further elementary processes research would be most beneficial, in acting as benchmarks against which simplified empirical chemistry results can be compared, and in evaluating the interactions of combustion chemistry within simple one-dimensional, time-transient systems with transport. The approach requires: (1) experimental effort for determining pyrolysis and oxidation intermediate and product profiles in a turbulent flow reactor; (2) comprehensive mechanism development and accompanying computer modeling; and (3) application of newly available sensitivity analysis computer tools to extract the maximum information from the first two parts of the research. Efforts are coordinated with sensitivity analysis research at Princeton, modeling efforts at Lawrence Livermore National Laboratory, and a fundamental kinetics program at Brookhaven National Laboratory. The experimental aspects of the project are conducted in a flow reactor facility developed at Princeton that permits chemical kinetic observations at atmospheric pressure, in the temperature range of about 900 to 1200 K, and for reaction times the order of 10 to 500 ms. The modeling aspects of the project are accomplished through use of several recently available computational tools (e.g., HCT, AIM, and CHEMSEN) and other tools and techniques as they become available. Chemical systems of current interest (in order of increasing complexity) are: the addition of small amounts of hydrocarbons to the $CO–H_2–O_2$ system, the formaldehyde pyrolysis and oxidation systems, the acetaldehyde pyrolysis and oxidation systems, and the pyrolyis and oxidation systems of simple alcohols.

### 227. *Aromatic-Radical Oxidation Kinetics*
*I. Glassman, K. Brezinsky* **$75,000**
*Department of Mechanical and Aerospace Engineering*

The realization that aromatics would be a major constituent in alternative fuels with significant attendant consequences on soot formation and fuel stability has provided a recent practical impetus for detailed studies of the combustion chemistry of these species. Such detailed understanding is necessary for combustor modelers and to assist in unraveling reasons for the great sooting tendency of aromatic compounds. We are initiating a series of atmospheric-pressure turbulent-flow-reactor experiments to elucidate the importance of oxygen atom addition to the aromatic ring and the displacement of a hydrogen from the ring during the high-temperature (1100 K) oxidation of benzene and toluene. $NO_2$, which, in a set of preliminary experiments, dramatically alters the oxygen atom concentration during oxidation experiments, will be used in a systematic manner to perturb the radical pool concentrations and influence intermediate species production. Phenol, a possible product of oxygen atom addition or hydrogen displacement by OH, will be the object of pyrolysis and oxidation experiments with and without $NO_2$ present. The judicious use of the additives NO, $N_2O$, and $(CH_3)_2CN(OH)$ during the oxidation studies will amplify the experimental results of the $NO_2$ studies.L

### 228. *Dynamical Studies of Molecular Systems*
*H.A. Rabitz* **$130,200**
*Department of Chemistry*

This project has two phases, consisting of studies in (1) chemical kinetics and (2) collision dynamics. In the first phase, 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 a special emphasis on combustion phenomena. Sensitivity techniques are being developed for probing the role of rate constants, transport coefficients, initial conditions, and boundary conditions on laboratory observables. The second phase of the research in collision dynamics is concerned with understanding the relationship between the structure of potential surfaces and resultant features in observable cross sections and rate constants. Both quantum mechanics and classical dynamics are being studied with emphasis on forward and inverse scattering processes. The ultimate aim of all the research is to understand the interrelationship between a hierarchy of microscopic and macroscopic observables in terms of fundamental potential interactions.

## Purdue University
## West Lafayette, Indiana 47907

### 229. *Measurement of Species Concentrations in Flames by Laser-Induced Fluorescence*
*N.M. Laurendeau* **$87,000**
*Department of Mechanical Engineering*

The primary objective of this research is to develop laser fluorescence methods for measuring the concentrations of flame species, including monatomic and diatomic radicals, diatomic and triatomic pollutants, significant polyatomic intermediates, and polycyclic aromatic hydrocarbons. The development of these methods will be a major advance in combustion diagnostics. An associated long-term research goal is to develop diagnostic techniques that will provide new understanding of (1) combustion kinetics, (2) the interaction between kinetics and turbulent flow, and (3) the influence of kinetics on the performance and emissions of practical combustion devices. We have (1) demonstrated quantitative laser-saturated fluorescence (LSF) measurements of both OH and NH concentrations, (2) developed a linear-fluorescence method for analyzing mixtures of polycyclic aromatic hydrocarbons (PAHs) in a vapor cell, and (3) progressed toward quantitative two-photon measurements of atomic hydrogen. Current research involves (1) continued application of laser-saturated fluorescence to the diatomic radicals CN, CH, and NO; (2) continued development of two-photon-induced fluorescence for atomic hydrogen and atomic oxygen; and (3) continued development of single-photon fluorescence for mixtures of polycyclic aromatic hydrocarbons. New research is proposed on (1) application of two-photon fluorescence to diatomic species such as NO; (2) development of two-photon fluorescence for mixtures of polycyclic aromatic hydrocarbons; and (3) extension of laser-saturated fluorescence to linear and nonlinear polyatomics.

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

### 230. *Kinetic Measurements on Elementary Fossil Fuel Combustion Reactions over Wide Temperature Ranges*
*A. Fontijn* **$70,400**
*Department of Chemical and Environmental Engineering*

This project objective is to provide kinetic data on important isolated elementary hydrocarbon molecule oxidation reactions. The high-temperature photochemistry (HTP) technique is used, which allows measurements to be made on such reactions in the 300 to 1800 K temperature regime in a single reactor. The pseudostatic reactor used provides an essentially wall-less reaction observation region. Reactions take place in a bath of heated argon. Experiments on the reaction between oxygen atoms and ethylene show a very sharp increase in the slope of ln k vs. $T^{-1}$ plots above about 1000 K, indicative of a major change in reaction mechanism. No other direct measurements of the rate coefficient for this reaction in the 1050 to 1500 K regime apparently exist. There is good agreement with other measurements below 1050 K, but the slope of the current data plot above 1000 K differs from that of a shock tube study, which covered the 1600 to 2300 K regime. Experiments on the reaction between oxygen atoms and acetylene have begun.

## Rice University
## Houston, Texas 77251

### 231. *Infrared Absorption Spectroscopy and Chemical Kinetics of Free Radicals*
*R.F. Curl, Jr., G.P. Glass* **$73,000**
*Department of Chemistry*

This research is directed at the detection, monitoring, and study of the chemical kinetic behavior of small free radical species (thought to be important intermediates in combustion) by infrared laser absorption spectroscopy. The infrared electronic spectrum of $C_2H$ and $C_2D$ is currently investigated to verify the previous vibronic assignments and locate the electronic origin. During the last few months, two infrared bands of $C_2D$ and one of $C_2H$ have been assigned and rotationally analyzed. In contrast with $C_2H$, vibronic coupling between the two lowest electronic states appears to be small for $C_2D$. Future spectroscopic studies planned include HCCN, $CH_2OH$, $CH_3O$, and $N_2H_3$. The kinetics and mechanisms of several reactions of free radicals in combustions will be investigated using free radicals and atoms produced by excimer laser flash photolysis and monitoring by infrared absorption spectroscopy. The reaction between $NH_2$ and NO has been investigated, and the branching ratio between OH product and $H_2O$ product channels has been determined. It is found that the major reaction channel produces $H_2O$ in very highly excited vibrational states. In future work, two kinds of reactions will be investigated: the reactions of oxygen atoms ($^3P$ and $^1D$) with acetylene and ethylene, and the reactions of $C_2H$ with acetylene and with $O_2$.

### 232. *Supersonic Bare Metal Cluster Beams*
*R.E. Smalley* **$81,000**
*Department of Chemistry*

A critical development in the emerging field of cluster beam studies of metal clusters has been achieved in the preparation of cold metal cluster ion beams. Using excimer laser irradiation of the clusters near the exit of the pulsed supersonic source, a cold plasma is produced containing both positive and negative metal cluster ions. Since this plasma is neutral overall, it receives the full cooling of the subsequent supersonic expansion. This technique has now been used in the first measures of (1) the adiabatic electron affinity of metal clusters (i.e., $Cu_x$) and (2) the binding energies of positive metal cluster ions and their fragmentation pathways, all as a function of cluster size. These new cluster beam methods are generally applicable to virtually all metal cluster systems, and a rich new body of information is expected to be obtained through their use.

## University of Rochester
## Rochester, New York 14627

### 233. *Low-Energy Ion–Molecule Reaction Dynamics and Chemiionization Kinetics*
*J.M. Farrar* **$77,900**
*Department of Chemistry*

Molecular beam reactive scattering measurements of proton transfer reactions of $H_3O^+$ and a number of reactions of the methyl cation $CH_3^+$ and the ground state carbon cation, including hydride abstraction and C–C bond formation reactions, have been studied with neutral molecules present in hydrocarbon flames with the goal of understanding the dynamics of ionic processes occurring in flames. We have completed studies of proton transfer reactions with $CH_3OH$ and acetone, with special emphasis on the unimolecular decay reactions that the nascent products undergo. Our recent work has focused on the low-energy dynamics of $C^+$ and $CH_3^+$ reactions with small molecules. The dynamics of $C^+$ reactions are dominated by insertion reactions into O–H and C–H bonds and the subsequent unimolecular decay of the transient insertion complex. $C^+$ appears to insert into the O–H bond of $H_2O$, forming a transient $CHOH^+$ intermediate that decays in one rotational period and allows us an estimate of the complex lifetime of 0.1 ps. Reaction of $CH_3^+$ with ethylene and acetylene involves C–C bond formation followed by loss of one or more H atoms or $H_2$ molecules. $CH_3^+$ also reacts with $C_2H_4$ to yield $C_2H_3^+$ in a complex process. Angular distributions provide information on complex decay geometries and lifetimes. Kinetic energy distributions provide information on intramolecular energy transfer. Isotope-labeling studies have been performed to assess H-atom scrambling in these systems. Other neutral reagents we have studied include $C_2H_6$, allene, and propyne. Condensation reaction dominates the dynamics of unsaturated hydrocarbons. Work in progress involves proton transfer reactions of $OH^-$ and electron detachment reactions of $O^-$ with small olefins, using multiphoton ionization to detect reaction products.

## University of Southern California
## Los Angeles, California 90089

### 234. *Chemistry of the Ethynyl Radical in Its $X^2\Sigma^+$ and $A^2\Pi$ States*
*C. Wittig* **$80,000**
*Department of Chemistry*

This research concerns elementary gas-phase processes of species important in combustion. We have developed a sub-Doppler resolution spectrometer for use with atomic hydrogen (Lyman-$\alpha$), which has the advantage of discriminating against species whose velocities are not collinear with the wave vector of the probing radiation. This enables kinetic energy distributions to be obtained, whereas conventional sub-Doppler resolution spectroscopy is incapable of providing such distributions. We have tested the method and verified our early predictions, and are now aiming at $\delta v/v < 0.01$. With this resolution, we will be able to resolve product vibronic excitation in many cases of the form $RH \rightarrow R + H$, at excess energies important in combustion. Data have been obtained for many precursors ($NH_3$, $C_2H_2$, $H_2S$, HBr, and HI) and in all cases S/N is high. In the case of $NH_3$, we show that internal excitation is very high (inverted) and cannot be determined by conventional spectroscopic methods such as LIF. By combining this probe with tunable vacuum-ultraviolet photolysis, we will be able to measure energy partitioning for a very large number of systems in which the radical fragments are "dark" to spectroscopic methods, albeit with energy resolution of only $\sim 100$ cm$^{-1}$. The method is also applicable to studies of clusters and bimolecular processes.

## SRI International
## Menlo Park, California 94025

### 235. *Combustion Research Program: Flame Studies, Laser Diagnostics, and Chemical Kinetics*
*D.R. Crosley* **$116,600**
*Molecular Physics Laboratory*

This research project involves a combination of laser-induced fluorescence (LIF) and chemical kinetics measurements to investigate the chemistry of hydrocarbon and ammonia combustion processes. The research comprises several related parts: (1) LIF probing of flat flames; (2) the development of an LIF spectroscopic and collisional data base; (3) computer modeling of combustion chemical networks; (4) development and application of rate constant estimation methods; and (5) a laser pyrolysis (LP)/LIF experiment. In LP/LIF, a mixture containing $SF_6$ is rapidly heated by a pulsed $CO_2$ laser, with time-resolved LIF measurements of radical concentrations, temperature, and excited level decay times. Measurements of the $OH + C_2H_2$ rate constant show an abstraction (addition) mechanism dominating above (below) 1000 K, agreeing with theoretical calculations of the combined pressure/temperature dependence of the addition channel. LP/LIF reaction rate measurements on OH + $CH_4$, $C_3H_8$, $C_3H_6$, and $NH_3$ have been made. Calculations on the $H + N_2O$ reaction and $CH_3 + CH_3$ recombination show bound intermediates and very different rate constant expressions from those currently used. The LIF spectroscopy of the $A^3\Pi_i–X^3\Sigma^-$ system of NH in a flow system has yielded lifetimes and transition probabilities. Quenching of the excited state has been studied at elevated temperature in the LP/LIF system.

Quenching of electronically excited OH by $NH_3$ has been studied at room temperature in a discharge flow system and at high temperature in LP/LIF. The LIF flame spectra of $NH_2$ in $NH_3$–$O_2$–$N_2O$ flames is being cataloged.

## Stanford University
## Stanford, California 94305

### 236. *Combustion Gas Spectroscopy Using Tunable Lasers*

*R.K. Hanson* **$76,000**
*Department of Mechanical Engineering*

This research is concerned with the development and application of tunable laser techniques for the measurement of fundamental spectroscopic parameters (absorption coefficients, oscillator strengths, fluorescence quench rates, and collision widths) for critical combustion species, particularly pollutants and radicals. Laser sources include a tunable CW infrared diode laser, a tunable CW ring dye laser, and a discretely tunable CO laser. Species studied include HCN, OH, NH, NCO, and CH. Measurements are made over a range of conditions in a controlled-temperature absorption cell, in the postflame region of a flat flame burner, and in a shock tube.

### 237. *The Kinetics of Cyano Compounds at High Temperature*

*R.K. Hanson, C.T. Bowman* **$77,000**
*Department of Mechanical Engineering*

The objective of this research project is to obtain high-temperature kinetic data for reactions involving HCN, CN, and NCO. These data are relevant to the formulation of reaction mechanisms for pollutant formation in flames. Reactions of interest include: (1) the reactions of HCN with O and OH; (2) the reaction of CN with OH; and (3) the reaction of NCO with OH. A conventional shock tube technique is combined with spectroscopic diagnostics to study the mechanisms and rates of candidate reactions. Experimental data are compared with results obtained from detailed kinetic models.

## University of Wisconsin
## Madison, Wisconsin 53706

### 238. *Unimolecular Reaction Dynamics*

*F.F. Crim* **$100,800**
*Department of Chemistry*

This project is an experimental study of the unimolecular decay dynamics of internal energy-selected molecules using direct production of highly vibrationally excited molecules by dye laser excitation of overtone vibrations in conjunction with time-resolved spectroscopic detection. Excitation of an overtone vibration prepares a molecule with a large excess of energy initially isolated in a small subset of the available vibrational modes. Time-resolved spectroscopic detection directly measures the unimolecular reaction rate constant and, in favorable cases, the energy partitioning in the products. Work includes excitation of CH and OH overtone vibrations and product detection using both visible chemiluminescence and laser-induced fluorescence. Chemiluminescence techniques directly measure the unimolecular decay rate of a selectively excited, ground electronic state molecule cooled in a supersonic expansion. In these measurements, a pulsed dye laser excites a cyclic peroxide (tetramethyldioxetane) in a molecular beam, and time-resolved detection of the product chemiluminescence provides the unimolecular decay rate. Laser-induced fluorescence experiments that detect the OH product of the vibrational overtone-initiated unimolecular decay of hydrogen peroxide (HOOH) reveal the partitioning of the excess energy among product quantum states and, through careful analysis of the vibrational overtone excitation spectra, uncover new details about highly vibrationally excited molecules. The newest work has observed the unimolecular reaction and vibrational predissociation spectrum of HOOH in a supersonic expansion. These studies test statistical theories of unimolecular reactions and provide data on the dynamics of isolated molecules potentially useful in understanding atmospheric chemistry, combustion processes, and laser-induced reactions.

## Wright State University
## Dayton, Ohio 45435

### 239. *Direct Determination of Atom and Radical Concentrations in Thermal Reactions of Hydrocarbons and Other Gases*

*G.B. Skinner* **$39,600**
*Department of Chemistry*

The general objective of this research is to study the kinetics of the atom and free-radical reactions important in combustion by following the appearance and disappearance of these combustion intermediates. Hydrogen, deuterium, and oxygen atoms are currently being measured in shock tube experiments using resonance absorption spectroscopy in the vacuum ultraviolet. The shock tube can operate over a range of 0.4 to 3 atm, so the dependence of reaction rates on total pressure can be studied. Our earlier measurements were in the 2 to 3 atm range, while recently we have studied several reactions near 0.4 atm. These include pyrolysis of benzene-$d_6$, toluene-$d_8$, $C_6H_5CD_3$, ethylbenzene and bromobenzene (in order to study dissociation of the phenyl radical), vinyl bromide, vinyl iodide, partially deuterated propenes, and the reaction of hydrogen atoms with acetylene-$d_2$. These are all key reactions in combustion chemistry.

## Yale University
## New Haven, Connecticut 06520

### 240. *Simultaneous Multipoint Measurements of Density Gradients and Temperature in a Flame*

*M.B. Long* **$60,000**
*Department of Mechanical Engineering*

Our research focuses on the development and application of nonintrusive optical techniques for making two- and three-dimensional measurements in turbulent reacting flows. A central theme has been to take advantage of developments in computer-controlled low-light-level imaging systems to provide data at a large number of spatially resolved points (typically 10,000). Recent efforts have led to the development of techniques that can measure the spatial characteristics of turbulent flows at framing rates high enough to follow the temporal evolution of structures. We have recently succeeded in obtaining a sequence of 320 two-dimensional measurements of the gas concentration in a turbulent flow at a framing rate of 1100 Hz. Another significant advance is the development of an imaging technique that can provide a measurement of the complete three-dimensional scalar gradient at each point within a plane intersecting the flow. The basis of this technique is to simultaneously and instantaneously illuminate the flow with two closely spaced parallel light sheets and to use two cameras with each camera detecting the image from a single illumination sheet. Data provided by these measurements can provide new information of direct interest to combustion modelers, such as the joint pdf of a scalar and its three-dimensional gradient.

# Atomic Physics

## Atlanta University
### Atlanta, Georgia 30314

*241. Theoretical Investigation of Electron–Ion Interaction*
*A.Z. Msezane* **$55,680**
*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 using the close-coupling approximation. Both total and differential cross sections are calculated and compared with measurements. In particular, detailed numerical studies are carried out to investigate the extent of contribution of the physical processes of inner-shell excitation-autoionization and inner-shell resonant excitation-double autoionization to the total ionization cross section of $Ti^{+3}$, important in CTR plasmas. Total and differential cross sections for electron impact excitation of magnesium(II) and cadmium(II), important in the He–Cd(II) hollow-cathode laser, are compared with measurements from energy loss spectrum and line emission data. An accurate configuration interaction wave function of the target is 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

*242. Correlated Processes in Atomic Collisions*
*J.M. Feagin* **$36,000**
*Department of Physics*

This project focuses on using progress in atomic physics in understanding Coulomb correlations in collisions. Work involves (1) transfer and excitation collisions and (2) Wannier threshold phenomena, and represents ongoing collaborations with several research groups, both theoretical and experimental, in the U.S. and Europe. The goal is to engage in calculations that closely confront theory with experiment in a simple direct way.

## University of Chicago
### Chicago, Illinois 60637

*243. Basic Studies of Atomic Dynamics*
*U. Fano* **$53,600**
*James Franck Institute*

This project aims at describing and predicting the correlations and energy transfers among the constituents of atoms and molecules, by identifying, evaluating, and exploiting the parameters that control critical processes. These processes are generally confined to limited volumes of space, often on top of potential barriers, serving as switchyards for wave function components that propagate smoothly (adiabatically) in different potential valleys. Recently we have concentrated on preliminary improvement of adiabatic wave functions in particular areas, based on adapting the coordinates and the functional form to local potentials. A separate task has dealt with a reformulation of collision theory that serves to disentangle its dynamics from experimental data.

## College of William and Mary
### Williamsburg, Virginia 23185

*244. Collisional Detachment of Negative Ions*
*R.L. Champion,* **$84,000**
*L.D. Doverspike*
*Department of Physics*

These experimental studies determine various cross sections to develop a general understanding of the collisional dynamics for systems that involve negative ions. The energy range of the experiments is from a few electron volts up to 500 eV. The experiments involve measurements of absolute total cross sections and doubly differential cross sections. The processes under investigation include collisional detachment, charge transfer, dissociative charge transfer, reactive scattering, and inelastic scattering. Emphasis is placed on elucidating the role of competing product channels in negative ion–molecule collisions and on delineating the various collisional processes that may occur in collisions of negative ions with atomic and molecular targets. Systems under investigation include hydrogen, deuterium, and alkali negative ions in collisions with hydrogen, deuterium, alkali atoms, $O_2$, $N_2$, CO, $CO_2$, $CH_4$, $NO_2$, and $SF_6$. The experimental results are coupled with theoretical models to provide a basis for understanding the role of negative ions in various environments.

## University of Colorado
### Boulder, Colorado 80309

*245. Spectroscopic Diagnostics of Electron–Atom Collisions*
*A.C. Gallagher* **$86,000**
*Joint Institute for Laboratory Astrophysics*

An experiment has been initiated to measure cross sections for electron excitation of metal atoms. The experiment is designed to yield differential cross sections for spin and angular momentum changes as a function of electron-scattering angle. The experimental plan uses laser excitation to high levels of atoms first excited by electron collision, and detection of the resulting fluorescence from a beam of atoms in a magnetic field. Each sublevel excited by the electrons is spectrally resolved, and partial cross sections for exciting each state are obtained from the optical excitation spectrum. The atomic recoil energy distribution resulting from the electron excitation is obtained from the Doppler shift of the absorption line from each substate. An apparatus has been constructed and tested. Measurements of Na $3S(M'_{s})$ arrow-right/ $3P(M_s,M_L)$ have been initiated, utilizing 3P → 5S excitation by a tunable laser. Excellent S/N has been obtained, and additional apparatus improvements are underway to allow accurate measurement of several electron–sodium cross sections.

### 246. *Near-Resonant Absorption by Atoms in Intense Fluctuating Fields*

*S.J. Smith* **\$88,490**
*Joint Institute for Laboratory Astrophysics*

This research is directed to the measurement of photon absorption by atoms immersed in very intense laser radiation fields near an atomic resonance. A primary objective is the accurate comparison of atomic absorption in a strong monochromatic field with the absorption in a strong field on which statistically well-characterized fluctuations are superimposed. A hybrid system of electro-optic and acousto-optic modulators is used to impose laser bandwidths up to 30 MHz and bandshapes out to 1 GHz from line center on a single-mode laser beam. Lineshapes ranging from Gaussian to Lorentzian are synthesized by controlling the time scale of the fluctuations. Measurements are in progress on the saturated $3S_{1/2}(F = 2, M_F = 2) \rightarrow 3P_{3/2}(F = 3, M_F = 3)$ transition in a highly collimated atomic sodium beam, using an optical double-resonance technique to study broadening, shifting, and splitting of the upper level as a function of laser intensity, detuning, and fluctuation parameters (linewidth and lineshape), where phase and frequency fluctuations are imposed. A separate study of effects of amplitude fluctuations in two-photon absorption has been initiated.

## Cornell University
## Ithaca, New York 14853

### 247. *Experimental Study of Interactions of Highly Charged Ions with Atoms at keV Energies*

*V.O. Kostroun* **\$245,000**
*Nuclear Science and Engineering Program*

This project involves the experimental study of interactions of very highly charged ions with atoms at low relative velocities. Emphasis is on collisions of bare hydrogen and helium-like projectiles with molecular hydrogen and helium. Fundamental quantities and processes of interest include (1) total capture cross sections as a function of incident ion energy, (2) partial cross sections for electron capture into specific states of the projectile, and (3) two-electron capture into autoionizing states of the projectile. The very highly charged ions will be furnished by the recently completed Cornell Electron Beam Ion Source, CEBIS, which produces such species by sequential electron impact ionization of ions trapped in an energetic, high-current-density electron beam. CEBIS is a superconducting solenoid cryogenic electron beam ion source, the first of its kind to be constructed in the U.S., currently undergoing tests and designed to produce initially bare argon ions at kinetic energy ≤2.25 KeV/nucleon. Longer range goals are to gradually upgrade the source to handle a 25 kV, 1 A electron beam that could be used to produce helium-like xenon. Thus far, a 4.5 kV, 0.5 A electron beam with a current density greater than 500 A/cm$^2$ has been propagated with 97% efficiency through the source at a 1.5 Tesla magnetic field. With this electron beam density at 10 kV, the source should be capable of meeting the initial design criteria for producing bare hydrogen and helium-like argon, ready for use in atomic physics experiments.

## University of Georgia
## Athens, Georgia 30605

### 248. *Quantum Mechanical Studies of Heavy-Ion Scattering Processes*

*T.G. Heil* **\$67,000**
*Department of Physics and Astronomy* **(15 mo.)**

This project concentrates on low- to intermediate-energy atomic collision processes where a quantum mechanical description is most appropriate. Several heavy-ion processes involving important constituent reactions that take place in terrestrial and astrophysical plasmas are studied in detail. Angular distributions have been calculated for heavy-ion collision processes that occur through potential curve-crossing mechanisms. These calculations show a new feature in the forward direction, near 0 degrees, with no semiclassical interpretations. A simple quantum mechanical model of the curve-crossing mechanism has been developed to explain this feature and features of existing semiclassical theories. This new model is based on fundamental parameters from the molecular theory of atomic collisions. Since it relates these parameters directly to differential scattering measurements, it allows for these parameters (nonadiabatic couplings) to be experimentally observed. The new model has an analytic semiclassical solution. Since it is based upon the most fundamental formulation of slow heavy-ion collisions, this new model may provide an alternative to more heuristic semiclassical curve-crossing models such as the Landau-Zener model. Charge transfer processes between neutral atoms and multiply charged ions are also studied at the *ab initio* level. Results are compared with experiments, with excellent agreement in most cases.

## Harvard University
## Cambridge, Massachusetts 02138

### 249. *Theoretical Studies of Highly Ionized Species*

*A. Dalgarno* **\$134,000**
*Harvard-Smithsonian Center For Astrophysics*

Theoretical studies have been carried out of proton impact and electron impact excitation of fine-structure transitions in the $n=2$ levels of hydrogenic ions. They are being extended to $n=3$ levels and to helium-like ions. The stability of multiply charged molecular ions has been investigated. A procedure for the variational calculation of the energies of ions in the Dirac-Hartree-Fock approximation has been developed. A multichannel theory of photodissociation has been worked out in diabatic formulation and applied initially to lithium fluoride.

## Jackson State University
### Jackson, Mississippi 39217

*250. Velocity Modulation Electronic Absorption Spectroscopy*
*B.C. Hale* **$55,000**
*Department of Chemistry*

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

*251. Theoretical Studies of Many-Body Processes in Atomic and Molecular Physics*
*S.I. Chu* **$65,300**
*Department of Chemistry*

The fundamental goals of this project are to develop new theoretical formalisms and practical numerical methods for probing intense field atomic and molecular multiphoton processes. Several new developments in semiclassical Floquet theory and quasi-energy methods are currently under investigation: (1) extension of conventional one-mode Floquet theory to the many-mode theory, allowing exact treatment of multiphoton excitation processes in the presence of more than one laser field; (2) nonadiabatic theory for studying resonant infrared multiphoton absorption spectroscopy; (3) most probable path approach for selecting the most important multiphoton excitation path, using artificial intelligence algorithms, allowing the study of multiphoton dynamics to very high order; (4) coupled dressed-quasi-molecular-states approach for the study of laser-assisted charge transfer reactions in slow ion–atom collisions; (5) SU(N) dynamical symmetries and symmetry breakings in multiphoton processes; and (6) Floquet-Liouville super-matrix approach to multiphoton resonance fluorescence and Raman scattering.

## Kansas State University
### Manhattan, Kansas 66506

*252. Atomic Physics of Strongly Correlated Systems*
*C.D. Lin* **$98,000**
*Department of Physics*

This project is directed toward the understanding of correlations and classification of two-electron atoms in hyperspherical coordinates and the development of practical computer codes for calculating inelastic cross sections in ion–atom collisions. The molecule-like rovibrational normal modes of doubly excited states are being studied within the hyperspherical methods. Two-center atomic orbital expansion method and a unified AO-MO matching procedure are being developed to study collisions at low energies for excitation and charge transfer processes in two-electron ion–atom collision systems. A quantum mechanical formulation is being developed in studying angular distributions of ion–atom collisions at low energies.

*253. Atomic Physics with Highly Charged Ions*
*P. Richard* **$855,000**
*Department of Physics*

High-velocity, highly charged ions produced by the 6 MV KSU tandem Van de Graaff accelerator are used to study charge transfer, ionization, and excitation in ion–atom collisions. Electron capture by highly charged ions is studied at very low projectile velocities using recoil ion sources. Single-electron capture by few-electron projectiles in He, $H_2$ and atomic hydrogen targets is being measured. Quasi-resonant multiple-electron transfer in near symmetric $F(_{q+})$ + Ne systems is also being measured. Measurements of total cross sections for multiple ionization by relativistic uranium ions were performed at the Berkeley BEVALAC. Translational energy gain spectroscopy for very-low-energy electron capture by neon and argon projectiles from atomic and molecular deuterium targets is used to determine final state (n,l) populations. The angular distributions for capture by similar projectiles from helium are being measured. The recoil ion source technology is being applied to the study of molecular ion chemistry. Exotic molecular ion species, ion lifetimes, and ion production rates are being studied. Theoretical calculations of the total cross section, nl distributions, and polarization from electron capture at high velocity are in progress. Calculations of theoretical lifetimes, transition energies, and branching ratios have been carried out for two-electron ions for configurations involving both electrons above the K shell.

## Louisiana State University
### Baton Rouge, Louisiana 70803

*254. Electron Collisions with Positive Ions*
*R.J.W. Henry* **$63,000**
*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. Calculations are made for inner-shell excitation-autoionization contributions to total ionization for magnesium-like $Al^+$, $S^{4+}$, $Cl^{5+}$, and $Ar^{6+}$ ions. The importance of indirect processes over the direct ionization process increases with increasing ionic charge along the sequence in agreement with experiment. Generalized oscillator strengths (GOS) for inelastic electron impact excitation of copper, $Zn^+$, and $Mg^+$ versus momentum transfer squared show some irregularities near $K^2 \rightarrow o$. This behavior renders measured GOC values unsuitable for normalization of experimental cross sections. Renormalization of copper measurements to our calculated GOS curves removes a factor-of-three discrepancy in the total cross section.

## University of Louisville
### Louisville, Kentucky 40292

*255. Spectroscopic Studies of Hydrogen Atom and Molecule Collisions*
*J. Kielkopf* **$68,275**
*Department of Physics*

This is an experimental laser-spectroscopic study of hydrogen atom and molecule interactions and the energetics and dynamics of molecular hydrogen collisions. The purpose of the study is to probe collisional energy transfer in the hydrogen molecule (and its isotopic variants), atom–molecule interactions, and the interactions of the hydrogen atom with noble gas atoms. Radiative collisions are analyzed, taking into account both binary and multi-perturber encounters, to find descriptions of the detailed processes that occur during collision. For the hydrogen atom, since its interaction with other atoms can often be calculated in detail, studies of the effects of the deviation from classical trajectories, interference due to the quantal nature of the collisions, collisional narrowing, and non-adiabatic transitions are possible. The project goal is to elucidate the basic collisional processes involving the hydrogen atom and the hydrogen molecule and the effects of neutral atom and molecule collisions on atomic spectral lines.

## University of Missouri/St. Louis
### St. Louis, Missouri 63121

*256. Low-Energy Ion-Neutral Collisions*
*J.J. Leventhal* **$68,000**
*Department of Physics*

This experimental project is designed to investigate energy transfer and energy conversion in atomic and molecular interactions. Current emphasis is on the study of interactions involving atoms in specific (laser-excited) electronic states and the study of ion–atom energy transfer in which energy disposal is effected by emission of visible and/or vacuum ultraviolet radiation. By using both spectral analysis of the radiation emitted by the reaction products and mass analysis of ionic products, nearly complete characterization of the interactions can be achieved. Of particular interest at this time is examination of the microscopic processes that collectively lead to macroscopic effects, such as plasma formation. The possibility of modifying these macroscopic effects using laser-induced chemistry is also being investigated.

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

*257. Atomic and Molecular Collision Processes*
*D.W. Norcross* **$96,000**
*Quantum Physics Division*

This project studies the physics of low-energy collisions of electrons with atoms, ions, and molecules, with an emphasis on detailed computational studies of fundamental processes involved in laser and fusion plasmas. Recent progress in the theory of electron–molecule collisions includes: (1) general code development to include nuclear dynamics and exchange effects more rigorously and to obtain bound states of molecular negative ions; (2) extension of earlier work on vibrational excitation of HCl to HF; (3) new calculations of vibrationally elastic scattering of positrons by CO; and (4) and studies of electron scattering by HCN in resonance symmetries. Our latest results for vibrational excitation of HF are in good agreement with measurements except at very near threshold, where complete treatment of nuclear dynamics is expected to remove remaining discrepancies. The facility to obtain energies of molecular negative ions will complement our results for resonance energies in HF and HCl, and in the isoelectronic molecules $N_2$, HCN, and CO. In the area of electron collisions with atomic ions, we have resolved a serious discrepancy between theory and measurements for excitation of $Be^+$ in favor of theory. It now appears that calibration techniques used in the measurements are seriously flawed.

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

*258. Electron–Atom Collision Studies Using Optically State Selected Beams*
*R.J. Celotta, M.H. Kelley* **$65,000**
*Radiation Physics Division*

The detailed information accessible to atomic collision experiments through the use of coherence, correlation, and polarization techniques is crucial for improving our understanding of collision phenomena. In particular, the observation of spin dependence in low-energy collisions between electrons and atoms is required to see directly the effects of spin exchange during collision. A crossed-beams scattering apparatus using optically state-selected beams has been constructed and is capable of very general studies of the scattering of spin-polarized electrons from spin-polarized atoms. This facility is used to study comprehensively the role played by electron spin in elastic, inelastic, and ionizing collisions. The current focus is spin dependence in superelastic scattering from excited atomic targets.

## University of Nebraska
### Lincoln, Nebraska 68588

*259. Hyperspherical Coordinate Theory of Two-Electron Processes*
*J.H. Macek, A.F. Starace* **$65,200**
*Department of Physics and Astronomy*

In this project electron correlations are studied in two-electron atoms, using theoretical methods employing hyperspherical coordinates. The doubly differential cross section for detachment of $H^-$ by impact with helium is studied using adiabatic hyperspherical coordinate initial and final state wave functions to compute the $H^-$ form factors. The detached electron's energy distribution is highly sensitive to the mean ionization potential of the target. The dipole matrix element for one-electron photodetachment of $H^-$ is computed in length and acceleration forms. The acceleration matrix element is found to be unreliable. A pseudostate method is developed to correct the gross inaccuracies of the adiabatic hyperspherical wave functions at large radial distances. This procedure yields significantly improved $^1S$ elastic phase shifts for electron scattering on atomic hydrogen. We have developed an asymptotic expansion of the adiabatic wave functions and eigenvalues for use at large radial distances. Our orbitals incorporate the long-range polarization of the target. An asymptotic solution of the coupled radial equations is also obtained. The Fock series expansion for two-electron wave functions has been successfully implemented numerically. When matched to single-channel adiabatic functions for some radius $R_0$, the Fock wave functions for helium and $H^-$ differ little (for $0 \leq R \leq R_0$) from the adiabatic wave functions, at least for the lowest adiabatic channels. WKB-type wave functions for the Wannier threshold region have been analyzed for negative total energies. A single Rydberg series of ridge-riding states is characterized by an energy-dependent effective charge and a slowly varying quantum defect. These states are resonances, and a formula for their resonance widths is obtained.

## New York University
## New York, New York 10003

### *260. Energy-Related Atomic and Molecular Structures and Scattering Studies*
*B. Bederson* **$76,000**
*Department of Physics*

Atomic, molecular, and cluster interactions with static and dynamic fields, and with low-energy electrons, are being studied. This work is partly motivated to elucidate the role played by long-range forces in atomic and molecular physics, and in cluster formation. After completion of the measurements of the electric dipole polarizabilities of all the alkali halide dimers we have reconstructed our polarizability machine, in preparation for an extension of these measurements to higher order alkali halide clusters. In a parallel experiment, the scattering of low-energy electrons by highly polar (alkali halide) molecules is being studied. We have recently performed preliminary measurements of very-small-angle scattering of electrons by CsCl and LiBr, where the monopole dipole interaction dominates. Our data reveals indications of structure in the differential cross sections, possibly attributable to interference between this interaction and higher order permanent and induced moment interactions. A supersonic source for cluster generation has been constructed, and is in use in the scattering experiments.

## University of North Carolina
## Chapel Hill, North Carolina 27514

### *261. Experimental Studies of Atomic Inner Shell Ionization Phenomena*
*S.M. Shafroth* **$73,000**
*Department of Physics and Astronomy*

This project is designed to study inner-shell vacancy production in ion–atom collisions, and subsequent decay via x rays or Auger electrons. K-shell dielectronic recombination cross section information is extracted by means of coincidence measurements between projectile K x rays and fast-moving projectile ions that have captured an electron while passing through a target gas at the appropriate velocity (resonant transfer and excitation). A background process that interferes with these measurements has been clarified (nonresonant transfer and excitation). Projectile K-electron excitation followed by K-x-ray emission and simultaneous electron loss has been studied. Target K-x-ray production and projectile ion electron capture and loss cross sections are measured. A high-efficiency electron spectrometer, capable of resolving closely spaced Auger electron lines emitted from fast-moving projectiles, has been built and tested. Electron angular distribution measurements are under way. A redesigned target chamber and beamline has been made operational at the Triangle Universities Nuclear Laboratory, where an FN tandem Van de Graaff produces fast-ion beams.

## Pennsylvania State University
## Lehman, Pennsylvania 18627

### *262. Electron Transfer, Ionization, and Excitation in Atomic Collisions*
*T.G. Winter* **$27,000**
*Department of Physics*

Electron transfer, ionization, and excitation in collisions of one atom (or ion) with another are studied theoretically. Emphasis is on accurate descriptions of collisional mechanisms for systems with few electrons; middle range of energies (keV) is considered. The projectile's speed is not very different from the average orbital speed of the active electron in the target atom (or ion). Therefore coupled-state methods are the most fruitful. The first calculation deals with collisions between protons and hydrogenic ions. A coupled-Sturmian-pseudostate approach is taken, which allows for continuum intermediate states that must be accounted for. Research for the hydrogenic ions $He^+$ and $Li^{2+}$ shows that the Sturmian approach yields very accurate descriptions of the collisions. This approach is being extended to the more highly charged ions $Be^{3+}$, $B^{4+}$, and so forth. Calculations will provide understanding of an entire set of fundamental collision processes not previously studied systematically, either theoretically or experimentally at keV energies.

## Purdue University
## West Lafayette, Indiana 47907

### *263. Nonlinear Optical Interactions Involving the Real Gaussian Field*
*D.S. Elliott* **$55,000**
*School of Electrical Engineering*

The goals of this project are (1) development of a technique for generating a laser field that realizes the real Gaussian field, characterized by a fluctuating amplitude that follows a Gaussian distribution; and (2) application of this field to a series of nonlinear optical transitions. This experiment will aid in understanding the effect of the finite bandwidth of a laser source on nonlinear optical transitions. This is a problem of considerable practical importance because nonlinear optical techniques using lasers of a variety of characteristics are routinely used for diagnostic, analytical, and spectroscopic applications, and the role of the properties of the laser radiation on these interactions is not understood. Results will be compared with a variety of theoretical works and with similar measurements based on the radiation of pulsed multimode lasers for which the knowledge of the statistical properties is incomplete. In addition, these results can be contrasted with experimental results of the same nonlinear interactions involving a phase-diffusion laser field.

## Rice University
## Houston, Texas 77005

### 264. *Theoretical Atomic and Molecular Sciences*
*N.F. Lane* **$105,600**
*Department of Physics*

Theoretical quantum-mechanical and semiclassical methods are used to investigate various atomic and molecular collision phenomena of fundamental interest and, in some cases, that are relevant to dense, high-temperature plasmas and other energy research environments. Current research projects include: (1) development and application of $L^2$ methods to Penning ionization of alkali atoms (and eventually clusters) in slow collisions with metastable helium atoms; (2) inelastic ion–ion and electron–ion scattering in dense, high-temperature fusion plasmas; (3) semiclassical studies of excitation and excitation transfer in slow collisions between highly excited atoms and molecules; (4) rovibrational excitation in electron–molecule collisions; and (5) excitation and charge transfer in ion–atom and ion–molecule collisions.

## University of Rochester
## Rochester, New York 14627

### 265. *Nonlinear Optics with Broad-Band Lasers*
*M.G. Raymer* **$90,000**
*Institute of Optics*

Experiments are being carried out to understand the statistical properties of broad-band laser radiation, and the effects of using such radiation in several areas of nonlinear optics. Intensity fluctuations and mode correlations are being studied in both cw and pulsed broad-band dye lasers via intensity autocorrelation and spectral measurements. Such broadband lasers are being used to pump stimulated Raman scattering in hydrogen gas. Intensity and field cross-correlations that develop between pump and probe laser beams in these processes are being observed, using an intensity cross-correlator. Evidence has been obtained for deterministic chaos in a continuous dye laser. This result may lead to an improved understanding of the intracavity laser spectroscopy technique.

## Smithsonian Astrophysical Observatory
## Cambridge, Massachusetts 02138

### 266. *Measurements of Ionization Balance Parameters in Atomic Ions*
*J.L. Kohl* **$98,900**
*Division of Atomic and Molecular Physics*

An inclined electron/ion beams experiment has been developed to measure absolute dielectronic recombination (DR) cross sections as a function of the applied electric field. The DR event rate is measured by detecting two products of DR in delayed coincidence: (1) the stabilizing photon and (2) the recombined ion. This technique discards events from charge transfer, which occur $10^7$ times more frequently than DR. Recent results for the energy-averaged DR cross section in $C^{3+}$ for a 10 V/cm external field indicates agreement with theoretical predictions to within a factor of two. This work provides the first opportunity to compare DR measurements for the species by two groups that use different experimental techniques. To establish the reliability of the apparatus for the DR experiments, the absolute detection efficiencies and the overlaps of the beams were verified with measurements of charge transfer and electron impact excitation. The results of these measurements agree with well-established experiment and theory.

## St. John Fisher College
## Rochester, New York 14618

### 267. *Multilevel Relaxation Phenomena and Population Trappings*
*F.T. Hioe* **$72,000**
*Department of Physics*

This research program undertakes to obtain a wide range of explicit analytic solutions for a variety of problems involving the multiphoton coherent excitation of multilevel quantum systems by intense laser beams. Various forms of amplitude and frequency-modulated laser beams have been considered. Simple conditions have been found that must be satisfied to achieve a complete population inversion or to achieve a complete population restoration. We have also found the conditions for certain systems to display population trapping. Studies of multiple pulse propagation through the multilevel media and of the problems of relaxation and spectrum will be made.

## University of Tennessee
## Knoxville, Tennessee 37996

### 268. *Production and Destruction of Metastable Negative Ions*
*D.J. Pegg* **$92,000**
*Department of Physics* **(24 mo.)**

The project objective is to investigate the production and destruction of metastable negative ions. A fast-moving beam of negative ions is produced from a beam of incident positive ions by double-electron capture collisions in an alkali vapor cell. We have investigated the production of $Ca^-$ ions following $Ca^+$ + Li collisions over a particle energy range from 20 to 100 keV. We have also used autodetachment spectroscopy to study the structure of metastable $Be^-$ and $He_2^-$ ions. In this work discrete energy electrons that spontaneously detach themselves in flight from fast-moving negative ions are collected in the forward direction and energy-analyzed in an electron spectrometer. Our measurements on the negative ion dimer, $He_2^-$, indicate that we are observing the breakup of this ion by two distinct mechanisms. Our future plans include studying the structure of alkaline-earth metastable negative ions such as $Ca^-$ by photodetachment spectroscopy.

## University of Texas
## Austin, Texas 78712

### 269. *Kinetic Studies Following State Selective Laser Excitation*
*J.W. Keto* **$83,000**
*Department of Physics*

Electronic energy transfer from xenon atoms and excimers is studied following selective excitation by multiphoton laser. Accurate electronic potentials for excimers are obtained by comparison of two-photon spectra with line-broadening theories and by direct measurement of rovibronic sequences of dimers in supersonic beams. In kinetic studies we are measuring excited state lifetimes, binary and ternary collisional quench rate, and state-to-state reaction rates. Recently published experiments studied intramultiplet transfer for $5p^56p$ xenon atoms. We are now studying reactive quenching of xenon atoms in collisions with chlorine molecules. We measure large reaction rates consistent with a harpoon model. These rates are important to current models of XeCl excimer lasers. In pure xenon samples, we have spectroscopically observed curve crossings in potential curves describing radiative collisions of xenon atoms. In similar experiments we are studying dissociation of excited Xe–$Cl_2$ and Xe–$I_2$ collision pairs.

## Texas A and M University
## College Station, Texas 77843

### *270. X-Ray Emission in Heavy-Ion Collisions*
*R.L. Watson* **$72,900**
*Cyclotron Institute*

Ionization, excitation, and electron transfer in high-energy heavy-ion collisions are investigated with high-resolution measurements of the photon radiation emitted during and after the collision process. The wavelength region of interest in these studies extends from the EUV up to x rays in the KeV range. Current experimentation is directed toward (1) the spectroscopy of few-electron ions, including the determination of x-ray polarization associated with aligned states produced in the collision process; (2) the study of delayed x-ray emission following beam-foil excitation; and (3) the systematic investigation of K x-ray satellite and hypersatellite structure, emphasizing the effects of rapid interatomic electron transfer.

## University of Toledo
## Toledo, Ohio 43606

### *271. Semiempirical Studies of Atomic Structure*
*L.J. Curtis* **$34,600**
*Department of Physics and Astronomy*

Studies of the structure and properties of very heavy and very highly ionized atoms that often occur as contaminants in high-temperature plasmas are carried out, using a combined program of experimental measurements, semiempirical data parameterizations, and *ab initio* computations. Spectroscopic classifications often require accuracies exceeding parts per million, which are not achieved by standard *ab initio* methods. Semiempirical systematizations can provide these accuracies, and a large and precise data base is available through recent studies using fast ion beam excitation, laser- and tokamak-produced plasmas, astrophysical sources, and conventional spectroscopic sources. These large blocks of data are being systematized and parameterized along isoelectronic, homologous, isoionic, Rydberg, and yrast series for the exposition of predictive empirical regularities. Trends revealed are then tested through well-chosen experimental measurements, and *ab initio* methods used to seek quantitative understanding of the empirical regularities. Recent work has stressed (1) spectra and (2) allowed and forbidden transition probabilities for states that are strongly affected by the inner core portion of the wave functions. This has revealed precise predictive regularities, which have been further investigated using the MFE CRAY X-MP computer for large-scale calculations of the highly specialized quantities, which were studied semiempirically.

## Vanderbilt University
## Nashville, Tennessee 37235

### *272. Theoretical Studies of Atomic Transitions*
*C. Froese Fischer* **$95,000**
*Department of Computer Science*

The present research is part of an ongoing project in atomic structure calculation, with special emphasis on the prediction of energy levels and transition probabilities as well as lifetimes. The method used is the MCHF method for including correlation effects in the wave function, optionally corrected for relativistic effects in the Breit-Pauli approximation. Transitions of current interest are the forbidden transitions that may be important in astrophysics for the electron density, or that have been observed in tokamak plasmas. Also of interest are the transitions between the doubly excited states of calcium(II), where predicted wavelengths and lifetimes are needed to identify lines of observed spectra. The present general purpose programs for the study of bound–bound transitions are being extended to include photoionization studies that may be characterized as bound–continuum transitions.

## University of Virginia
## Charlottesville, Virginia 22901

### *273. Studies of Autoionizing States Relevant to Dielectronic Recombination*
*T.F. Gallagher* **$83,200**
*Department of Physics*

A novel laser excitation method is used to excite alkaline-earth atoms in an atomic beam to autoionizing states that decay into an ion and a free electron. The processes are precisely the inverse of the dielectronic recombination of ions and electrons through autoionizing states, and thus allow detailed measurements of the basic physical processes important in dielectronic recombination. Dielectronic recombination is an important power-loss process in tokamak plasmas, and these results have real practical value. The total autoionization rates are measured directly as a function of the principal and angular momentum quantum numbers and as a function of applied electric fields. The angular and energy distributions of the ejected electrons are measured and yield the autoionization rates into specific states of the ion and outgoing electrons. All together these measurements allow us to obtain the detailed microscopic atomic data that enter into the process of dielectronic recombination.

## Western Michigan University
## Kalamazoo, Michigan 49008

### *274. Correlated Charge-Changing Ion–Atom Collisions*
*E.M. Bernstein, J.A. Tanis* **$65,200**
*Department of Physics*

The project objective is to probe fundamental atomic interactions in collisions between ions and atoms. Individual processes of excitation, ionization, and charge transfer, and certain combinations of these processes, are investigated for highly charged ions incident on neutral gas targets by correlating projectile charge-changing events with K x-ray emission. This work uses accelerators at Lawrence Berkeley Laboratory, Brookhaven National Laboratory, Argonne National Laboraguidelines for the molecular engineering of new and better catalysts for the production of fuels and other organic products from CO and other small molecule substrates.

### 279. *Reactions of Iron Atoms with Molecules in Low-Temperature Matrices*

*R.G. Pearson, P.H. Barrett* **$77,800**
*Department of Chemistry*

The goal of this project is to study the reactivity of metal atoms and small clusters with molecules in low-temperature matrices. Mossbauer and infrared spectroscopies are used to identify the reaction products. Reactions between iron, $Fe_2$, and iron clusters, and low-temperature matrix-isolated molecules of $N_2$, NO, CO, $C_2H_4$, $SO_2$, and $C_6H_6$ have been studied and the products identified. This investigation includes the search for bond-cleaving reactions of HX, some of which have been found. Reactions of $CH_3X$ and $O_2$ are also under study.

## California Institute of Technology
## Pasadena, California 91125

### 280. *Fundamental Studies of Olefin and Acetylene Insertion Reactions*

*J.E. Bercaw* **$124,000**
*Department of Chemistry* **(19 mo.)**

This project involves fundamental studies of the mechanism and thermodynamics of olefin and alkyne insertion into metal–hydrogen and metal–carbon bonds. The reactions of olefins with hydride and alkyl derivatives of metallocenes of the general formula $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R$ and $(\eta^5\text{-}C_5R'_5)_2M(\text{olefin})H$ (R = H, alkyl, alkenyl, alkynyl; R′ = H,Me; M = Nb,Ta) have proven to be very clean and amenable to mechanistic studies. Relative ground state energies for $(\eta^5\text{-}C_5R'_5)_2M(\text{olefin})H$ (M = Nb,Ta; R′ = H, $CH_3$) have been determined by competitive binding studies. The molecular structure of $(\eta^5\text{-}C_5Me_5)_2Nb(CH_2CHC_6H_5)H$ has been determined by x-ray crystallography. Relative transition state energies have been established by measuring the insertion rates as a function of the olefin and steric contributions from the metallocene (R′ = Me vs. H). The kinetics of stepwise insertion of ethylene into the scandium–carbon bond of $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R$ (R = alkyl) have been examined by $^{13}C$ NMR spectroscopy. The reaction of $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R$ (R = Me) with alkynes, $RC{\equiv}CR'$ (R = Me; R′ = Me,Et,Ph,*i*Pr) and decomposition of $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R$ (R = Et,*n*Pr) via β-hydrogen elimination are being probed with $^1H$ NMR spectroscopy. These processes (olefin insertion into the metal–hydride bond, its inverse, β-hydride elimination, and the related process of insertion of olefins into the metal–alkyl bond) are among the most important steps in homogeneously catalyzed reactions of olefins.

### 281. *Catalytic Assembly of Hydrocarbons from Carbon Monoxide*

*R.H. Grubbs* **$115,000**
*Department of Chemistry*

This research is concerned with the activation and reduction of carbon monoxide and the development of models for the assembly of hydrocarbons on multimetal catalysts. Group VI-B intramolecular metalloesters are synthesized from cationic transition-metal(II) carbonyl complexes, using intramolecular nucleophiles. Spectroscopic and x-ray crystallographic evidence confirms the general structure as an ester derived from the attack of an alkoxide at a carbonyl ligand. Equilibrium studies indicate that attack by an intramolecular nucleophile may be favored over that of an intermolecular one depending on the structure linking the nucleophile to the metal center. The optimum linker configuration and oxidation state for intramolecular nucleophilic attack is investigated. A family of Group IV ketene complexes has been synthesized as models for C–C coupling intermediates in CO reduction reactions. Of particular interest are hetero-binuclear complexes that show a wide range of reactivities and structures. The first case of a trigonal bipyrimidal $CH_3M_2$ complex has resulted from these studies. A large number of $M\text{–}CH_2$ complexes have been prepared and demonstrated to undergo a variety of C–C coupling reactions.

## University of Chicago
## Chicago, Illinois 60637

### 282. *Reactions of Electrophilic Reagents with Bituminous Coals: The Chemistry of the Reaction Products*

*L.M. Stock* **$87,500**
*Department of Chemistry*

We have studied the ruthenium(VIII)-catalyzed oxidation of coal. The phenolic and etheral aromatic molecules are selectively oxidized in this process to yield simpler structures. The products obtained in the oxidation of 25 representative molecules have been determined, and the products from seven representative coals have been studied by nuclear magnetic resonance and mass spectrometry. Quantitative methods based on isotopic dilution techniques have been worked out and applied successfully for the determination of the alkyl groups in coals and other prominant structural features. This information has been used to establish the structural characteristics of these coals. The electrophilic substitution reactions of bituminous coals are also under investigation. The mercuration and plumbylation reactions have been carried out successfully for the first time. Plumbylated Illinois No. 6 coal undergoes oxidative solvolysis to yield a material selectively enriched in aryl hydroxyl groups. This altered coal undergoes donor solvent liquefaction in tetralin to yield products that are more soluble in hexane than the natural materials. This work is providing a more secure basis for the discussion of the role of hydroxyl groups in coal conversion reactions.

## University of Colorado
## Boulder, Colorado 80309

### 283. *Studies of Hydrogen–Hydrogen and Carbon–Heteroatom Bond Cleavage Reactions*

*M.R. DuBois* **$58,000**
*Department of Chemistry and Biochemistry*

The molybdenum dimer $(C_5H_5Mo\mu\text{-}S)_2S_2CH_2$, I, serves as a homogeneous catalyst for the hydrogenolysis of vinyl halides and of other organic halides. The reaction of Complex I with β-bromostyrene has been investigated in the absence of hydrogen. A β-phenyl vinylthiolate bridged complex of the formula $[(C_5H_5Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCHC(Ph)H)]Br$, II has been isolated and characterized by an x-ray diffraction study. The vinylthiolate ligand of the cation is oriented in an equatorial position. Complex II undergoes a series of reactions with hydrogen (1 to 2 atm) at 40°C. Intermediates have been identiguidelines for the molecular engineering of new and better catalysts for the production of fuels and other organic products from CO and other small molecule substrates.

### *279. Reactions of Iron Atoms with Molecules in Low-Temperature Matrices*

*R.G. Pearson, P.H. Barrett* **$77,800**
*Department of Chemistry*

The goal of this project is to study the reactivity of metal atoms and small clusters with molecules in low-temperature matrices. Mossbauer and infrared spectroscopies are used to identify the reaction products. Reactions between iron, $Fe_2$, and iron clusters, and low-temperature matrix-isolated molecules of $N_2$, NO, CO, $C_2H_4$, $SO_2$, and $C_6H_6$ have been studied and the products identified. This investigation includes the search for bond-cleaving reactions of HX, some of which have been found. Reactions of $CH_3X$ and $O_2$ are also under study.

## California Institute of Technology
## Pasadena, California 91125

### *280. Fundamental Studies of Olefin and Acetylene Insertion Reactions*

*J.E. Bercaw* **$124,000**
*Department of Chemistry* **(19 mo.)**

This project involves fundamental studies of the mechanism and thermodynamics of olefin and alkyne insertion into metal–hydrogen and metal–carbon bonds. The reactions of olefins with hydride and alkyl derivatives of metallocenes of the general formula $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R$ and $(\eta^5\text{-}C_5R'_5)_2M(\text{olefin})H$ (R = H, alkyl, alkenyl, alkynyl; R′ = H,Me; M = Nb,Ta) have proven to be very clean and amenable to mechanistic studies. Relative ground state energies for $(\eta^5\text{-}C_5R'_5)_2M(\text{olefin})H$ (M = Nb,Ta; R′ = H, $CH_3$) have been determined by competitive binding studies. The molecular structure of $(\eta^5\text{-}C_5Me_5)_2Nb(CH_2CHC_6H_5)H$ has been determined by x-ray crystallography. Relative transition state energies have been established by measuring the insertion rates as a function of the olefin and steric contributions from the metallocene (R′ = Me vs. H). The kinetics of stepwise insertion of ethylene into the scandium–carbon bond of $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R$ (R = alkyl) have been examined by $^{13}C$ NMR spectroscopy. The reaction of $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R$ (R = Me) with alkynes, $RC{\equiv}CR'$ (R = Me; R′ = Me,Et,Ph,*i*Pr) and decomposition of $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R$ (R = Et,*n*Pr) via β-hydrogen elimination are being probed with $^1H$ NMR spectroscopy. These processes (olefin insertion into the metal–hydride bond, its inverse, β-hydride elimination, and the related process of insertion of olefins into the metal–alkyl bond) are among the most important steps in homogeneously catalyzed reactions of olefins.

### *281. Catalytic Assembly of Hydrocarbons from Carbon Monoxide*

*R.H. Grubbs* **$115,000**
*Department of Chemistry*

This research is concerned with the activation and reduction of carbon monoxide and the development of models for the assembly of hydrocarbons on multimetal catalysts. Group VI-B intramolecular metalloesters are synthesized from cationic transition-metal(II) carbonyl complexes, using intramolecular nucleophiles. Spectroscopic and x-ray crystallographic evidence confirms the general structure as an ester derived from the attack of an alkoxide at a carbonyl ligand. Equilibrium studies indicate that attack by an intramolecular nucleophile may be favored over that of an intermolecular one depending on the structure linking the nucleophile to the metal center. The optimum linker configuration and oxidation state for intramolecular nucleophilic attack is investigated. A family of Group IV ketene complexes has been synthesized as models for C–C coupling intermediates in CO reduction reactions. Of particular interest are hetero-binuclear complexes that show a wide range of reactivities and structures. The first case of a trigonal bipyrimidal $CH_3M_2$ complex has resulted from these studies. A large number of $M\text{–}CH_2$ complexes have been prepared and demonstrated to undergo a variety of C–C coupling reactions.

## University of Chicago
## Chicago, Illinois 60637

### *282. Reactions of Electrophilic Reagents with Bituminous Coals: The Chemistry of the Reaction Products*

*L.M. Stock* **$87,500**
*Department of Chemistry*

We have studied the ruthenium(VIII)-catalyzed oxidation of coal. The phenolic and etheral aromatic molecules are selectively oxidized in this process to yield simpler structures. The products obtained in the oxidation of 25 representative molecules have been determined, and the products from seven representative coals have been studied by nuclear magnetic resonance and mass spectrometry. Quantitative methods based on isotopic dilution techniques have been worked out and applied successfully for the determination of the alkyl groups in coals and other prominant structural features. This information has been used to establish the structural characteristics of these coals. The electrophilic substitution reactions of bituminous coals are also under investigation. The mercuration and plumbylation reactions have been carried out successfully for the first time. Plumbylated Illinois No. 6 coal undergoes oxidative solvolysis to yield a material selectively enriched in aryl hydroxyl groups. This altered coal undergoes donor solvent liquefaction in tetralin to yield products that are more soluble in hexane than the natural materials. This work is providing a more secure basis for the discussion of the role of hydroxyl groups in coal conversion reactions.

## University of Colorado
## Boulder, Colorado 80309

### *283. Studies of Hydrogen–Hydrogen and Carbon–Heteroatom Bond Cleavage Reactions*

*M.R. DuBois* **$58,000**
*Department of Chemistry and Biochemistry*

The molybdenum dimer $(C_5H_5Mo\mu\text{-}S)_2S_2CH_2$, I, serves as a homogeneous catalyst for the hydrogenolysis of vinyl halides and of other organic halides. The reaction of Complex I with β-bromostyrene has been investigated in the absence of hydrogen. A β-phenyl vinylthiolate bridged complex of the formula $[(C_5H_5Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCHC(Ph)H)]Br$, II has been isolated and characterized by an x-ray diffraction study. The vinylthiolate ligand of the cation is oriented in an equatorial position. Complex II undergoes a series of reactions with hydrogen (1 to 2 atm) at 40°C. Intermediates have been identified by NMR spectroscopy and synthesized independently by alternate routes. They include $[(C_5H_5Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH(Ph)CH_3)]Br$, III, and $(C_5H_5Mo)_2(S_2CH_2)$(mu/-$SCH(Ph)CH_3)_2$, IV. Reaction paths for the formation of the intermediates have been characterized. Complex IV reacts with hydrogen (1 to 2 atm, 40°C) to form ethyl benzene and Complex I to complete the catalytic cycle. The series of reactions establish that the hydrogenolysis of the carbon–halide bond of vinyl halides proceeds through the formation and subsequent hydrogenolysis of carbon–sulfur bonds in the dimeric molybdenum complexes. The reactions provide relevant homogeneous models for the chemistry that occurs on heterogeneous hydrotreating catalysts.

### 284. *Chemisorption and Reaction Studies on Well-Characterized Bimetallic and Alloy Surfaces*

*B.E. Koel* **$65,000**
*CIRES Department*

The project objective is to explore the chemisorption and reactions of hydrocarbons on well-characterized bimetallic and alloy surfaces. A wide range of bimetallic surfaces composed of a Group VIII metal and another metallic element will be studied in order to gain a better fundamental understanding of the role of electronic and geometric effects in modifying the chemistry of these surfaces. Results will aid in the atomic level explanation of the reactivity and selectivity of alloy and bimetallic cluster catalysts. We will obtain fundamental data for the adsorption and decomposition of hydrocarbons and other small molecules on single-crystal bimetallic surfaces that have been well-characterized using Auger and photoelectron spectroscopy and low-energy electron diffraction. The structure and bonding of adsorbed molecules will be studied by vibrational spectroscopy using high-resolution electron energy loss spectroscopy and by temperature-programmed desorption. We will be able to correlate changes in chemisorption bond strengths, adsorption site distributions, and hydrocarbon fragment stability and reactivity with the geometric and electronic structure of the metal atoms on the bimetallic surface.

## Colorado State University
## Fort Collins, Colorado 80523

### 285. *Chemically Modified Electrodes and Related Solution Chemistry*

*C.M. Elliott* **$77,000**
*Department of Chemistry*

In this research we are investigating chemically modified electrodes and related solution chemistry. The goal is to alter the chemical and/or physical properties of the electrode–solution interface in useful ways. Our primary emphasis is the development of polymer-coated electrodes containing electroactive materials. Several such electrodes have been prepared. In the course of studying fundamental processes of electron and ion transport in such modifying polymers, we have developed a new type of electronically conducting "organic" polymer, which is presently under study. There are two aspects to our studies of chemically modified electrodes: (1) developing schemes for incorporating electroactive systems of interest into polymers and (2) developing and studying molecules of potential interest (e.g., catalysts) 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. A number of novel metalloporphyrins have been prepared, and their redox chemistry is under investigation both in solution and polymer bound. Other polymers under study 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.

### 286. *Diosmacycloalkanes as Models for the Formation of Hydrocarbons from Surface Methylenes*

*J.R. Norton* **$67,000**
*Department of Chemistry*

This project has developed several efficient general syntheses of diosmacycloalkanes. The project will next determine the extent to which these compounds can: (1) serve as models for methylene aggregation on the surface of Fischer-Tropsch catalysts; (2) catalyze olefin metathesis; and (3) rearrange carbon skeletons. The properties of these compounds will be compared to those of their mononuclear analogs, in order to determine which (if any) steps in typical catalytic sequences require the presence of polynuclear systems. We have shown that, in contrast to the established chemistry of cyclobutane rings without metals, olefins exchange in and out of diosmacyclobutanes with retention of stereochemistry at carbon. The project will also see if hydrocarbon C–H bonds can be activated by $Os(CO)_4$ or any other species generated photochemically from $Os(CO)_5$.

### 287. *Heterobimetallic Complexes for Carbon Monoxide Reduction*

*J.K. Stille* **$73,000**
*Department of Chemistry*

The project goal is to synthesize certain homogeneous heterobimetallic catalysts (containing both an early and a late transition metal) that will reduce carbon monoxide selectively under mild reaction conditions. Because several heterogeneous catalysts (either mixed metal oxides or mixed alloy catalysts) reduce carbon monoxide under relatively mild conditions more selectively than a catalyst composed of only one metal, heterobimetallic catalyst synthesis will be emphasized. Complexes containing combinations of early (niobium, molybdenum) and late (iron, cobalt, rhodium) transition metals that could be expected to activate carbon monoxide most effectively are primary targets. Complexes containing iron methyl and tungsten methyl held together by a bridging ligand (cyclopentadienyldiphenylphosphine) have been synthesized and characterized (x-ray) as well as a complex containing iron methyl and tungsten hyride, which undergoes reductive elimination to yield methane. Complexes containing niobium and rhenium bridged by connected cyclopentadienyl ligands also have been synthesized. By the synthesis of such heterobimetallic catalysts and the observation of the interaction of the ligands on the two metal centers, the answers to some fundamental mechanistic questions surrounding the individual steps in the reduction of carbon monoxide should be attained.

## University of Connecticut
## Storrs, Connecticut 06268

### 288. *Highly Dispersed Metal Atoms in Zeolites*
*S.L. Suib* **$70,000**
*Department of Chemistry*

We are studying the effects of metals in zeolite catalysis, including the preparation of highly dispersed metal atom clusters in zeolites, surface and bulk characterization of metal-loaded zeolites, and the study of metal poisoning of high-activity commercial fluid cracking catalysts. Highly dispersed cobalt and iron samples have been prepared; characterized by ferromagnetic resonance and Mossbauer and x-ray photoelectron spectroscopy; and are selective Fischer-Tropsch catalysts for small molecular weight olefins. Superparamagnetic Fe(0) and Co(0) clusters smaller than 9 A have been produced and characterized with electron microscopy and $H_2$ chemisorption experiments. X-ray photoelectron spectroscopy and Rutherford backscattering methods were used to distinguish surface and bulk metal species in zeolites. Chemical state plots were assembled for aluminophosphate and silicoaluminophosphate molecular sieves and showed that Auger and photoelectron lines for silicon and aluminum are related to oxygen ion polarizabilities and, therefore, to the degree of covalency of Si–O and Al–O bonds in these zeolites. Metal poisoned fluid cracking zeolite catalysts were studied with luminescence methods; results suggest that vanadium poisons leach oxygen from the zeolite whereas nickel sinters and acts to overcrack gasoline hydrocarbons to coke, $H_2$, and light gases. Further studies show that iron resembles nickel, whereas copper mimics vanadium.

## University of Delaware
## Newark, Delaware 19716

### 289. *A Surface Science Investigation of Potential Intermediates, Catalysts, and Promoters in the Synthesis of Higher Alcohols by Metals*
*M.A. Barteau* **$68,000**
*Center for Catalytic Science and Technology*

The goal of this project is to provide the fundamental knowledge required to extend recent advances in methanol synthesis catalysis to the development of selective noble metal catalysts for the synthesis of higher alcohols. The hypothesis is that surface alkoxide species are pivotal intermediates in the synthesis of higher alcohols. This study examines the formation, stability, and reactivity of these intermediates on clean and modified surfaces of rhodium and palladium to determine the properties of these metals that lead one (rhodium) to be active for synthesis of higher alcohols. Results obtained on the Pd(111) surface have demonstrated that CO is eliminated from surface alkoxides to form hydrocarbons containing one less carbon atom than the parent aliphatic alcohol. The presence of surface oxygen enhances the thermal stability of adsorbed methoxide species, but destabilizes higher alkoxides by permitting oxidation and dehydrogenation pathways. These results help to explain reaction mechanisms and promoter effects in alcohol synthesis.

## Harvard University
## Cambridge, Massachusetts 02138

### 290. *Model Studies of Hydrodesulfurization and Hydrodenitrogenation on Sulfided Molybdenum Surfaces*
*C.M. Friend* **$71,300**
*Department of Chemistry*

Model hydrodesulfurization reactions of four-carbon cyclic and linear sulfur-containing molecules have been investigated on Mo(110) under ultrahigh vacuum conditions using temperature-programmed reaction spectroscopy, isotopic exchange reactions, and Auger electron spectroscopy. Thiophene exclusively undergoes irreversible C–H bond activation on Mo(110). At low coverage, all thiophene decomposition occurs below 400 K. At high coverage, thiophene undergoes selective dehydrogenation at the $\alpha$ position with a hydrogen-bearing fragment stable on the surface up to 570 K. No volatile hydrocarbon products are observed in the thiophene reaction. In contrast, the fully saturated $C_4S$-ring, tetrahydrothiophene, yields butane and butene in the temperature range of 300 to 420 K. The activation energy for butane formation is approximately 5 kcal/mole less than for butene formation. Analogous reaction with the same energetics is observed for 1-butane thiol on the Mo(110) surface with a product yield that is roughly five times greater than for thiophene. These results suggest a mechanism for thiophene reaction on Mo(110) where one of the $\alpha$-carbons is initially hydrogenated with accompanying C–S bond scission, producing an intermediate analogous to 1-butane thiol. Hydrogenation at the other $\alpha$-carbon yields butane while $\beta$-hydride elimination forms 1-butene. Deuterium coadsorption experiments substantiate this mechanism, in that one deuterium is incorporated into the butane and no deuterium into the butene formed from reaction of 1-butane thiol on Mo(110).

## University of Illinois
## Chicago, Illinois 60680

### 291. In Situ *Ultraviolet Diffuse Reflectance Studies of Heterogeneous Catalysis*
*R.D. Gonzalez* **$106,500**
*Department of Chemical Engineering* **(18 mo.)**

The project objective is to develop an *in situ* ultraviolet technique to study structural changes in surface phases under reaction and preparative conditions. Three separate problems will be studied using this *in situ* technique: (1) the dynamics of the metal particle nucleation process during the synthesis of supported metallic and bimetallic catalysts, (2) self-sustained oscillations in the CO oxidation reaction over $Pt/Al_2O_3$ and $Pd/SiO_2$, and (3) the role played by surface chlorides in the enhanced adsorption of CO in the presence of coadsorbed hydrogen on $Ru/Al_2O_3$ catalysts. The use of ultraviolet diffuse reflectance spectroscopy will be complementary to infrared spectroscopy as a surface probe. Infrared spectroscopy can yield useful information only regarding the structure of the chemisorbed adlayer, while ultraviolet diffuse reflectance spectroscopy is capable of probing the surface layer. We have selected the studies outlined above because we feel that important questions remain unanswered and that by following changes in the surface phases of the working catalyst we can perform a series of definitive experiments.

## Indiana University
## Bloomington, Indiana 47405

### 292. *Model Cu–ZnO Catalysts for Methanol Synthesis: The Role of Surface Structure*

*C.T. Campbell* **$100,000**
*Department of Chemistry* **(18 mo.)**

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 ($CO + 2H_2 \rightarrow CH_3OH$). We believe such information will guide the design of improved catalysts for this important reaction. Our approach involves model catalysts prepared from single-crystal copper or by vapor-depositing copper onto low-index planes of a ZnO single crystal. In this way a range of well-defined surface electronic and geometric models of the Cu–ZnO catalysts can be prepared. These structures will be characterized in ultrahigh vacuum using a variety of surface analytical techniques immediately before and after high-pressure kinetic measurements, which are used to determine the activity of the model catalysts. The influence of surface modifiers and the kinetics of elementary reaction steps will also be studied. By correlating surface structure and composition with the observed rates, we should begin to develop a fundamental understanding of the surface chemical requirements for effective catalyst design.

### 293. *Metal Alkoxides: Models for Metal Oxides*

*M.H. Chisholm* **$80,000**
*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 $\sigma^2$ and $(\sigma^2 + \pi^2)$ donors allows for easy uptake and release of substrate molecules. Key observations during the 1984 to 1986 period are: (1) the cleavage of $C{\equiv}O$ to carbido- and oxo-tungsten alkoxide clusters; (2) the coupling, co-coupling, and sometimes metathesis-like reactions ($M = W$) between $C{\equiv}C$, $C{\equiv}N$, and $M{\equiv}M$ bonds in $M_2(OR)_6$ compounds; (3) unusual $\beta$-hydrogen effects in dinuclear alkylalkoxides of molybdenum; and (4) the isolation of Mo–Mo quadruply bonded compounds supported by alkoxide ligands. Recent developments have led to general synthesis of hydridoditungsten alkoxide anions $W_2(\mu\text{-}H)(OR)_8^-$, which have been isolated as sodium salts. New nitrido and amido clusters have been discovered, $Mo_4(\mu_3\text{-}N)_2(OPr^i)_{12}$ and $W_3(\mu_3\text{-}NH)(OPr^i)_{10}$, which may provide models for the Haber synthesis of $NH_3$ from $N_2$ and $H_2$. Routes to alkyl/aryl-containing tri- and tetranuclear alkoxide clusters have been developed.

### 294. *Free Radical and Concerted Reactions in Coal Liquefaction*

*J.J. Gajewski, K.E. Gilbert* **$75,000**
*Department of Chemistry*

This project focuses on fundamental mechanistic problems involved in the thermal reactions of hydroaromatic compounds, as a basis for understanding the chemistry of coal liquefaction. We have found that 1,3-diarylhydrocarbons and ethers decompose by free-radical chain processes at 300 to 400°C, that these reactions may be initiated at lower temperatures, and may be inhibited by phenols up to 200°C. The kinetic and thermodynamic barriers to these reactions have been studied. We have found that phenyl-substituted tetralins cleave to smaller fragments and rearrange by a complex series of radical reactions that are very inefficient. We have also found that alkenes can be hydrogenated to alkanes by a stepwise radical process in good hydrogen donor solvents, but react to form dimers by a concerted process in poor hydrogen donor solvents. Finally, a computer program to accurately calculate the structures and heats of formation of conjugated $\pi$ electron systems has been developed. It is achieving widespread use in academic and government laboratories.

## Indiana University–Purdue University
## Indianapolis, Indiana 46223

### 295. *Studies of Metal–Ammonia Interactions with Aromatic Substrates*

*P.W. Rabideau* **$66,000**
*Department of Chemistry*

Reduction and reductive alkylations effected by electron addition in dissolving metal systems such as sodium or lithium in liquid ammonia can provide an important method for the solubilization of coal and studies of coal structure. This research is aimed at a better understanding of the fundamental nature of this reaction using aromatic and polynuclear aromatic compounds as model structures. Recently, dimeric methylated naphthalene derivatives have been used as coal models; it has been determined that the presence of a second polynuclear ring system does not inhibit reduction of the first, but rather it seems to promote it. The significance is that a first-approximation coal can be thought of as a large number of polynuclear ring systems linked together by carbon chains. The intermediates in these reactions are being studied directly by carbon and proton nuclear magnetic resonance techniques, and indirectly by protonation sites and alkylation stereochemistry. The conformational analysis of the reduced products (partially reduced six-membered rings) is also being studied by NMR techniques as well as theoretically with force field calculations.

## University of Kentucky
## Lexington, Kentucky 40506

### 296. *Metallacumulenes and Carbide Complexes*

*J.P. Selegue* **$108,000**
*Department of Chemistry* **(20 mo.)**

We are studying the synthesis, structure, and reactivity of metallacumulenes and carbide complexes, containing cumulated chains of carbon–carbon double bonds terminating at transition metal atoms at one or both ends. The reaction of $[Fe(C{=}CHMe)(Ph_2CH_2CH_2PPh_2)(Cp)]^+$

($Fp'=C=CHMe^+$) with iodosobenzene or cupric acetate gives an oxidized divinylidene product [$Fp'=C=C(Me)C(Me)=C=Fp'$]$^{2+}$, with formation of a carbon–carbon bond. Secondary allenylidene complexes [$Ru(C=C=CHFc)(PR_3)_2(Cp)$]$^+$ (Fc = ferrocenyl; R = Me, Ph) are formed by the reaction of $HC=CH(Fc)(OH)$ with [$RuCl(PR_3)_2(Cp)$]. The formation of allenylidene and vinylvinylidene complexes are competitive processes, as illustrated by reactions of $HC=C(OH)(CH_2)_5$ with [$RuCl(PR_3)_2(Cp)$] (R = Ph, Me) that lead to [$Ru\{C=C=C(CH_2)_5\}(PPh_3)_2(Cp)$]$^+$ and [$Ru\{C=CHC=CH(CH_2)_4\}(PMe_3)_2(Cp)$]$_+$. Steric factors probably determine which product is formed. Related studies of molybdenum and tungsten complexes that clarify the relationship between alkyne and vinylidene ligands are under way. Our products serve as models for carbon-rich fragments formed on metallic catalyst surfaces during synthesis gas and acetylene conversion reactions.

## Lehigh University
## Bethlehem, Pennsylvania 18015

### 297. *Infrared Study of Carbon Deposits on Bimetallic Catalysts*

*R.P. Eischens* **$88,000**
*Department of Chemistry*

The project objectives are to determine the nature of carbon deposits on alumina-supported bimetallic catalysts and to determine whether the species that produce infrared bands at 1585 and 1460 cm$^{-1}$ are related to the enhanced productivity of bimetallic catalysts. Preliminary results were interpreted on the basis that bands observed at 1585 and 1460 cm$^{-1}$ were due to carbon–oxygen bonds even though the deposition of coke by exposure of the catalysts to hydrocarbons was conducted under reducing conditions. Later interpretations by other researchers assigned the 1585 cm$^{-1}$ band to the carbon–carbon stretching mode in aromatic rings and the 1460 cm$^{-1}$ band to a $CH_2$ deformation. The first phase involves isotopic substitution studies designed to definitively establish the nature of the species producing the 1565 and 1460 cm$^{-1}$ bands. The second phase will involve studies of a number of bimetallic catalyst systems and the effect of sulfur to determine whether the species producing the 1585 and 1460 cm$^{-1}$ are especially detrimental to the performance of the kinds of catalysts used in pertroleum-reforming processes.

### 298. *Mechanisms and Controlling Characteristics of the Catalytic Oxidation of Methane*

*K. Klier, G.W. Simmons,* **$161,000**
*R.G. Herman, J.E. Strum*
*Department of Chemistry* **(18 mo.)**

The object of this research is to lay scientific foundations for processes used for the selective oxidation of methane to useful energy chemicals and basic chemicals. Recent effort focused on a surface science study of the palladium(100)–oxygen–dichloromethane–methane system using a LEED/Auger/mass spectrometer. Pd/O and $Pd/CH_2Cl_2$ reactions were characterized in detail, while $Pd/CH_4$ reaction was not detected at pressures below $10^{-6}$ torr and temperatures below 1000 K. Recent results of Auger lineshape analysis show that surface chlorine from dichloromethane adsorption is atomic in nature. Subsequent exposure of dissociatively adsorbed dichloromethane to oxygen with mild heating leads to the removal of all surface carbon in the form of CO and $CO_2$ (hydrogen apparently desorbs at room temperature) leaving the surface chlorine unchanged, unless heated above 1000 K, whereupon chlorine desorbs. Importantly, the surface chlorine coverage shows a correlation with the CO, $CO_2$, and $O_2$ desorption temperatures and their relative amounts, suggesting that chlorine affects the oxidation of the carbon-containing fragments. Reacting methane with Pd/Cl, Pd/O, and $Pd/CH_2Cl_2$ surfaces is under study. A recently completed HREEL spectrometer is being used to identify surface species associated with the reaction of $CH_2Cl_2$ with palladium and subsequent reactions of this surface with oxygen and methane.

### 299. *Polymer-Based Catalysts*

*S.L. Regen* **$126,000**
*Department of Chemistry* **(24 mo.)**

This research is aimed at developing new and improved polymer-based catalysts and selective chemical transformations. Specific chemical objectives include: (1) the entrapment of metal colloids within porous and nonporous polymerized vesicles and an examination of their resulting activity, stability, and size-selectivity toward alkene hydrogenation, (2) the incorporation of soluble transition metal complexes within polymerized vesicle membranes and the measurement of their ability to promote region- and size-selective catalytic hydrogenation, (3) the construction of receptor sites within polymerized vesicle membranes, and (4) the extension of the "vacillating-reaction" principle to catalytic systems.

## University of Louisville
## Louisville, Kentucky 40292

### 300. *Synthesis and Properties of Metallocarboxylic Acids*

*D.H. Gibson* **$79,500**
*Department of Chemistry*

This research involves the study of several groups of metallocarboxylic acids, with the goal of determining the scope of reactions characteristic of this class of compounds and the steric and electronic factors that promote the reactions. Alternative synthetic routes of metallocarboxylic acids will be examined that do not involve hydroxide ion addition to a metal carbonyl group. Peroxymetallocarboxylic acid derivatives, which may serve as models for other carbon monoxide oxidations, will be prepared and their chemistry investigated.

## Massachusetts Institute of Technology
## Cambridge, Massachusetts 02139

### 301. *Reduction of Carbon Monoxide*

*R.R. Schrock* **$180,000**
*Department of Chemistry* **(18 mo.)**

The objective of this research is to learn how to reduce carbon monoxide catalytically and selectively to a two-carbon product such as ethanol, ethylene glycol, ethylene, or acetaldehyde. We have turned our attention to complexes containing two metals linked by a peralkylated cyclopentadienyl ring system (e.g., $Me_4C_5CH_2CH_2C_5Me_4$), especially those containing tungsten and a group 8 or 9 metal such as cobalt, rhodium, or ruthenium. The objective is to prepare heterobimetallic hydrido complexes that will react with CO in a unique fashion due to the early/late metal combination. Such species are unlikely to be prepared by classical techniques. Our approach involves the formation of one of the cyclopentadienyl ring systems from a tungstenacyclobutadienyl ring system. We have recently discovered a high-yield route to the simplest of these, a trimethyl-substituted ring system, in four simple steps starting from tungsten hexachloride. We are beginning to prepare heterobimetallic complexes in quantities large enough (several grams) to allow us to systematically explore their chemistry.

## University of Minnesota
## Minneapolis, Minnesota 55455

### *302. Direct Alcohol Synthesis on Cobalt-Modified Catalysts*
*G.L. Griffin* **$70,000**
*Department of Chemical Engineering and Materials Science*

We are studying the adsorption and reaction properties of Cu–ZnO, Co–ZnO, and Co–Cu–ZnO catalysts intended for the direct synthesis of methanol and higher alcohols from CO:$H_2$ mixtures. Our prinicpal goals are (1) to understand the adsorption behavior of highly dispersed metals in ZnO-based catalysts and (2) to determine the importance of these adsorption sites in alcohol synthesis reactions. Results obtained during the first year for the binary Cu–ZnO system indicate that for submonolayer coverages of copper (e.g., less than $10^{15}$ copper atoms/$m^2$ of ZnO), the copper species are present in an electron-deficient (i.e., partially oxidized) metallic state. This state is characterized by abnormally high values for the vibrational frequency of adsorbed CO, and by a significant barrier to oxygen adsorption. The methoxy and formate intermediates produced during methanol decomposition are more stable on these supported copper surfaces than on bulk copper. These copper species are also quite active for $CH_2O$ hydrogenation, which indicates that the rate-limiting step in methanol synthesis is instead the hydrogenation of the formate intermediate. Work is in progress to determine whether copper maintains this electron-deficient state under alcohol synthesis conditions, and whether a similar state also occurs for cobalt supported on ZnO.

### *303. Photochemical Properties of Transition Metal–Arene Complexes*
*K.R. Mann* **$66,000**
*Department of Chemistry*

The photochemical reactivity of transition metal–arene complexes will be studied by examining the mechanisms of the arene replacement reactions by NMR, laser flash photolysis, and classical mechanistic techniques. The intermediate species generated in these reactions will be utilized as catalytic photoassistance agents, and in the synthesis of novel organometallic complexes.

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

### *304. Structure and Reactivity of Chemisorbed Species and Reaction Intermediates*
*T.E. Madey* **$147,000**
*Surface Science Division*

This project addresses the structure and reactivity of adsorbed molecules on single-crystal catalysts and on high-area catalysts using a variety of experimental methods. Recent research has involved four areas with a common theme, the investigation of surface processes related to catalytic chemistry. The role of surface additives (oxygen, bromine, alkali atoms) on the local structure and surface chemistry of small molecules ($NH_3$, $H_2O$, CO) adsorbed on single-crystal metal surfaces (ruthenium, iron, nickel, silver) was studied using the electron stimulated desorption ion angular distribution (ESDIAD) method. The additives often were found to induce new structural forms of the adsorbed molecules and reaction products. The adsorption and decomposition of CO and $O_2$ on a chromium(110) surface were characterized using ESDIAD and high-resolution electron energy loss spectroscopy (EELS); molecular precursors to decomposition were found in both cases, and their structures were characterized. Neutron inelastic scattering (NIS) was used to measure the vibrational spectra of hydrogen and hydrocarbons adsorbed on surfaces of platinum-black and zeolite catalysts. The poisoning of CO hydrogenation reactions by sulfur was studied over single-crystal tungsten(110) catalysts. Evidence for primarily short-range interactions was found.

## University of North Carolina
## Chapel Hill, North Carolina 27514

### *305. The Heats of Formation of Gas Phase Organo-Sulfur Molecules and Applications of $^{17}O$ and $^{33}S$ NMR to Structure Determinations*
*T. Baer, S.A. Evans, Jr.* **$120,000**
*Department of Chemistry* **(18 mo.)**

This project emphasizes photoionization and heteronuclear nuclear magnetic resonance (NMR) techniques to determine structures and energetics of organosulfur molecules. The $\Delta H_f^o$ of the series: RS · [R = $CH_3$, $CH_3CH_2$,$(CH_3)_2CH$, and $(CH_3)_3C$] are measured. In addition, the $\Delta H_f^o$ of various sulfonyl compounds are determined by bomb calorimetry to make these substances amenable for photoionization studies. Chemical oxidation of sulfenyl sulfur (–S–) to sulfones ($-SO_2-$) and particularly, to sulfonic acids ($-SO_3H$) serves to quench the quadrupolar broadening effect. This allows for development of an analytical NMR technique for the rapid and accurate analysis of sulfur in organosulfur constituents in coal and petroleum extracts. Polar substituent effects on $^{33}S$ chemical shifts in aryl sulfones and sulfonic acids are evaluated, as well as the possible use of magic-angle spinning techniques for determination of $^{33}S$ shift parameters in the solid state.

### *306. Reductive Coupling of Carbon Monoxide to $C_2$ Products*
*J.L. Templeton* **$58,000**
*Department of Chemistry*

Two approaches to reductive C–C bond formation between adjacent carbon monoxide ligands at a single metal center are being pursued. The first (recently validated by Lippard of by others) employs external reductants in an effort to reductively couple *cis*-carbonyl ligands to form $[OC \equiv CO]^{-2}$. The acute OC–M–CO angles of seven-coordinate $d^4$ metal carbonyl derivatives and the six-coordinated $d^4$ alkyne containing products are uniquely suited for this chemistry. The second approach focuses on the conversion of a terminal CO to a pseudocarbyne by protonation (or Lewis acid addition) at the oxygen to generate an effective hydroxycarbyne *cis* to a carbonyl. Examples of carbyne–carbonyl coupling have been reported, and we hope to promote a similar internal redox process by addition of acid and free ligand to convert $d^6$ $L_4M(CO)_2$ to $L_4L'M(HOC \equiv COH)$ or a Lewis acid analog.

## Northwestern University
## Evanston, Illinois 60201

### 307. *Solid-State, Surface, and Catalytic Studies of Oxides*
*H.H. Kung* **$93,200**
*Department of Chemical Engineering*

This project elucidates the interrelation among the solid-state, surface, and catalytic properties of oxides. The relation between surface structure and surface chemistry was studied with temperature-programmed decomposition of organic oxygenates on different crystal surfaces of ZnO. Simultaneous with the decomposition of the organic molecules, zinc atoms were desorbed at temperatures lower than the sublimation temperature. The extent of the zinc atom desorption differed for different surfaces (with the most on the zinc-polar face) and for different molecules. Methanol was the most effective. The desorption was suppressed by the presence of gaseous oxygen. It was proposed that the desorption was due to reduction of the ZnO surface, which became a surface similar to one of ZnO with deposited zinc metal. This zinc metal was desorbed at temperatures lower than the sublimation temperature of ZnO. The solid properties of the catalyst that affect the selectivity in the oxidation of hydrocarbons are analyzed by considering the mechanistic steps in the oxidation reaction. It was reasoned that the breaking of the C–H bonds in alkanes is facilitated by weakly adsorbed oxygen. The C–H bond breaking of alkenes is enhanced by strongly basic surface lattice oxygen, and cations that are soft acid and that undergo redox readily. Desorption of alkenes and dienes is enhanced by cations that are hard acid. The selective C–O bond formation is controlled by the number and ease of removal of the available lattice oxygen. The combustion reaction can be minimized by shortening the residence time of the surface intermediates, weakening the adsorption of the desired products, and minimizing the amounts of weakly adsorbed oxygen on the combustion sites.

### 308. *Supported f-Element Organometallic Complexes: Surface Chemistry and Catalysis*
*T.J. Marks, R.L. Burwell, Jr.* **$86,000**
*Department of Chemistry*

The project objective is to elucidate, via a coordinated chemical and spectroscopic investigation, the nature of species produced when organo-f-element complexes (and by inference, early transition metal complexes) are adsorbed on high-surface-area metal oxides. These species constitute some of the most active olefin hydrogenation catalysts yet discovered and are also highly active for ethylene polymerization. Catalytic hydrogenation studies have now expanded from initial $Cp'_2MR_2$/propylene systems ($Cp' = (CH_3)_5C_5$, M = Th,U) to other olefins (for $Cp'_2MR_2$ catalysts, $N_t$: propylene $\simeq$ 1-butene $\gg$ isobutylene), metal complexes ($N_t$: $Cp'MR_3 \gg Cp'_2MR_2 > Me_2Si[(CH_3)_4C_5]_2MR_2 \gg Cp_3MR$), and supports (for $Cp_2MR_2$ catalysts, $N_t$:dehydroxylated $Al_2O_3$ > partially dehydroxylated $Al_2O_3$ $\gg$ dehydroxylated $SiO_2$). Mechanistic studies have included deuterium labeling, CO poisoning, and preliminary kinetic measurements. A number of other complexes, catalytic reactions, and supports are also under examination. Closely integrated with this effort are high resolution CPMAS $^{13}C$ NMR studies of the adsorbed molecules. Using isotopic labeling, differing magnetic fields, and various pulse techniques, it is possible to obtain significant adsorbate structural and dynamic information at less than monolayer coverages. We have also demonstrated the applicability of this technique to elucidating metal carbonyl surface chemistry.

### 309. *Chemical Interactions in Bimetal/Zeolite Catalysts*
*W.M.H. Sachtler* **$90,600**
*Department of Chemistry*

The industrial application of transition metals, supported by zeolites, is limited by the weak metal/support interaction of these systems, which results in poor dispersion maintenance of the metal under severe conditions. The primary project objective is to increase the dispersion maintenance by introducing a chemical anchor for the noble metal. We have found that the cations $Fe^{2+}$ and $Cr^{3+}$, when exchanged into a NaY zeolite, markedly improve the dispersion of platinum. One test is to first oxidize $Pt(NH_3)_4^{2+}$/NaY in $O_2$, increasing the temperature from 20 to 550°C and then to reduce the metal with $H_2$ at 550°C. After this severe treatment the platinum particle size is measured by x-ray diffraction (XRD) and $H_2$ chemisorption. Both methods reveal a significant anchoring effect of $Fe^{2+}$ and $Cr^{3+}$ ions; in their absence large XRD peaks of platinum are recorded, but with $Fe^{2+}$ no platinum XRD signal can be detected, and a superior dispersion is maintained after 100 hours in $H_2$ at 500°C. Benzene hydrogenation revealed that the platinum catalyzed reaction rate was dramatically increased. This increase in rate exceeded the increase in platinum dispersion by a factor of seven. We are using EXAFS to investigate the interaction between noble metal particles and anchoring ions. We plan to use other transition metal ions and other test reactions (conversion of n-hexane or methyl-cyclopentane) to identify the dual action of transition metal ions as anchors and catalyst promoters.

### 310. *Structure and Chemistry of the Interaction of Organometallics with Surfaces*
*D.F. Shriver* **$143,700**
*Department of Chemistry* **(18 mo.)**

One objective of this research is to characterize organometallics attached to surfaces to elucidate the cluster–support interaction. Parallel model studies of organometallic compounds in solution and of conventionally prepared heterogeneous catalysts are performed to obtain a coherent picture of fundamental organometallic chemistry related to CO activation by heterogeneous catalysts. Based on our previous experience with the chemistry of CO in homogeneous solution chemistry, we have postulated that electropositive metals promote CO cleavage and migration insertion reactions. Therefore, we are studying supported mixed-metal clusters that contain one electropositive metal (e.g., Rh–Fe clusters on metal oxide surfaces by infrared and EXAFS techniques). The catalytic chemistry of these same materials is under investigation.

## University of Pennsylvania
## Philadelphia, Pennsylvania 19104

### *311. Desorption and Reaction Kinetics Studied on Model Supported Catalysts*
*R.J. Gorte* **$75,700**
*Department of Chemical Engineering*

Temperature programmed desorption (TPD) and reaction studies are being carried out on model catalysts in which small particles of a metal (platinum, rhodium, or palladium) are deposited on top of an oxide, or a thin film of oxide is deposited on top of a metal. For metals on oxides, the particle size is characterized from adsorption coverages of CO or $H_2$. The catalytic properties of these samples, including adsorption properties and reaction rates for ethane hydrogenolysis, are then measured as a function of particle size and oxide composition. For small metal particles, initial results indicate that the distribution of crystal planes on the particles are affected by the substrate composition and the particle size. For oxides on metals, results indicate that some oxides tend to "wet" the metal surface while others form clusters.

### *312. Catalytic Hydrogenation of Carbon Monoxide*
*B.B. Wayland* **$105,000**
*Department of Chemistry*

The project objective is to learn how to use the unique properties of rhodium porphyrins in achieving catalytic hydrogenation of carbon monoxide at mild conditions. Rhodium porphyrins react with $H_2$ and CO at pressures less than one atomsphere to produce a metalloformyl complex that is a primary intermediate in the hydrogenation of CO. Several catalytic schemes are proposed that take advantage of the unique reactivity of rhodium porphyrins coupled with the aldehydelike character of the metalloformyl intermediate. Multifunctional catalysts that use rhodium porphyrins and a second catalyst known to promote the hydrogenation of aldehydes are particularly promising candidates for achieving low-pressure hydrogenation of CO. Solvent effects are explored as one means of tuning the thermodynamic and kinetic parameters for optimum catalytic behavior. Results from studies of the rhodium prophyrin system provide a guide in designing new materials that retain the favorable thermodynamic factors, but have improved reaction kinetics. Comparative studies using variation of the ligand array and central metal (cobalt, rhodium, iridium) are used to optimize the desired catalyst behavior.

## Pennsylvania State University
## University Park, Pennsylvania 16802

### *313. Mechanistic Studies of Carbon Monoxide Reduction*
*G.L. Geoffroy* **$110,000**
*Department of Chemistry*

The reactivity of methylene, ketene, and imido ligands on metal clusters is being explored. Recent studies have revealed the facile carbonylation of methylene ligands to produce ketene ligands, with a significant halide-promoting effect for this reaction. The ketene ligand has been subsequently converted into enolate, vinyl, and acetyl ligands by reactions with electrophiles and nucleophiles. Current focus is on developing the synthetic chemistry of such coordinated ketene ligands. The coupling of imido ligands on clusters with carbenes, acyls, methoxycarbonyl, and alkyne ligands has been observed to give a variety of organic products. Halide ligands also promote these reactions; the basis for this unique halide-promoting effect is currently under study.

### *314. Determination of the Distribution of Hydrogen in Coal by FTIR*
*P.C. Painter* **$90,000**
*Department of Materials Science and Engineering*

The project objective is to measure the distribution of hydrogen in coal according to functional group, which will provide considerable insight into coal structure, particularly for those coals for which $^{13}C$ NMR values of the fraction aromatic carbon content are also available. Fourier transform infrared spectroscopy (FTIR) is the principal tool used in this investigation. Although this technique has been applied to coal characterization for a number of years, results reported by various groups differ considerably. Accordingly, a major part of the initial research focuses on determining the precision of the numbers that can be obtained.

### *315. Transition Metal Catalyzed Transformations of Unsaturated Molecules*
*A. Sen* **$156,000**
*Department of Chemistry* **(24 mo.)**

The homogeneous catalysis of organic transformations by transition metal compounds is of considerable practical and scientific 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 homogeneous catalytic systems and (2) to use this knowledge to develop new and useful catalytic processes. The two catalytic systems under current study are: (1) the palladium(II)- and rhodium(I)-catalyzed copolymerization and cooligomerization of olefins with carbon monoxide and (2) the palladium(II)-catalyzed tail-to-tail dimerization of alkyl acrylates. For the former system, our studies elucidate the unique chain growth mechanism that leads to the formation of the copolymers. Further mechanistic studies lead to a detailed understanding of the individual steps involved in the chain growth sequence and allow us a greater control of the molecular weight and the end groups of the copolymers. With regard to the latter catalytic system, studies of model systems led to the discovery of new patterns of reactivity that may be related to the mechanism of the actual catalytic process.

### *316. Characterization of Catalysts with Metal-Support Effects and of the Species Adsorbed on Their Surfaces*
*M.A. Vannice* **$95,000**
*Department of Chemical Engineering*

The project objective is to elucidate the chemistry involved in the creation of metal-support interactions that have pronounced effects on adsorption and catalytic behavior in certain systems. Focus is on characterizing adsorbed molecules and the chemical and physical state of the metal and support. The project involves a study of heats of adsorption for $H_2$, CO, and $O_2$ on platinum, palladium, and nickel using a modified differential scanning calorimeter combined with a thermal gravimetric analysis unit and separate chemisorption experiments. Kinetic investigations will be made on hydrogenation reactions involving aromatic hydrocarbons and the C–O bond in carbon monoxide and acetone. Scanning transmission electron microscopy will be used to better define the state of the metal particles and the particle size distributions. Solid-state magic angle spinning NMR will be used to study adsorbed $^{13}C$-labeled CO and hydrocarbons and to conduct Knight shift experiments on the metal itself ($^{195}Pt$) to determine the influence of the support on conduction electrons. This multifaceted approach attempts to explain the much higher catalytic activities found in certain reactions and the suppressed chemisorption sometimes observed after a high-temperature reduction. A recently proposed model invoking special active sites created at the metal support interface will be carefully examined. Heats of adsorption of $H_2$, CO, and $O_2$ on palladium follow a similar trend: they all increase significantly on palladium crystallites below 3 nm, and the support has little effect. A similar, less pronounced pattern occurs for $H_2$ on platinum, but the support (such as $TiO_2$) can markedly decrease CO $\Delta H_{ad}$ values on platinum.

## University of Pittsburgh
## Pittsburgh, Pennsylvania 15261

### *317. Carbidic Ad-Layer as Rate-Controlling Factor in CO–$H_2$ Catalysis*

*P. Biloen* **$85,000**
*Department of Chemical and Petroleum Engineering*

The project objective is to assess the reactivity and abundance of reaction intermediates present at the surface of CO-$H_2$ converting catalysts during steady-state catalysis. The central question is to what extent carbonaceous side products control the abundance of reaction intermediates. In a typical experiment, the isotopic constitution of the feed is changed abruptly (e.g., $^{12}CO–H_2 \rightarrow {}^{13}CO–H_2$). This leads to a transient phenomenon: the displacement of $^{12}C$ by $^{13}C$, first in the catalyst ad-layer and then in the product. The rates of displacement contain transient-kinetic information regarding the abundance and reactivity (i.e., lifetime) of reaction intermediates. With $^{12}CO$ and $^{13}CO$ exhibiting essentially identical reactivity, the steady-state of the system is essentially not affected by the isotopic switch. Key findings are: (1) convergence in intermediates are not controlled by surface-blocking side products, but rather by intrinsic kinetic and surface properties; (2) activity decline on aging is driven by changes in catalytic properties of the surface rather than by surface blocking (both statements pertain to nickel-derived catalysis in a specific operation window); and (3) differences in transient behavior between platinum and nickel provide evidence that methanation over nickel proceeds via carbidic intermediates.

### *318. Studies of Supported Metal Catalysts*

*D.M. Hercules* **$90,300**
*Department of Chemistry*

We have investigated the effect of additives on the early stages of catalyst preparation (i.e., impregnation), by examining the effect of additves on the isoelectric point (IEP) of the alumina support and the ensuing impact on the adsorption of metal complexes from solution. We have examined the influence of additives known to promote the HDS reaction (boron, titanium) on the state and dispersion of $Mo/Al_2O_3$ and $Co/Al_2O_3$ catalysts. A method has been developed to use ESCA to determine the speciation of oxidic alumina-supported metal catalysts, and has been used to study the speciation of $Co/Al_2O_3$ catalysts. The results were consistent with published cobalt speciation data derived from Mossbauer spectroscopy. Laser Raman spectroscopy (LRS) was used to identify and quantitate the species present in CoMo/TiO catalysts, which cannot be readily quantified by other analytical techniques.

### *319. Infrared Studies of Influence of Alkali Metals on C–O Bond in Chemisorbed Carbon Monoxide*

*J.T. Yates* **$271,700**
*Department of Chemistry* **(24 mo.)**

This research project is designed to probe the interaction of adsorbed alkali metals and electronegative poisons with adsorbed carbon monoxide on transition metal single-crystal surfaces. Information obtained by reflection infrared spectroscopy, x-ray, photoelectron spectroscopy, and temperature-programmed desorption will yield models of the interaction, and deeper understanding of the alkali promotion effects and electronegative poisoning effects observed in catalytic chemistry on transition metals. Recently, the range of S poisoning on a nickel(111) single crystal has been determined, and the nature of K···CO interactions have been probed in detail. A mixture of short- and long-range effects are observed.

## Purdue University
## West Lafayette, Indiana 47907

### *320. Reduction of Aromatic Compounds Derived from Coal by Calcium*

*R.A. Benkeser* **$65,000**
*Department of Chemistry*

Previously we disclosed that calcium dissolved in ethylenediamine (or in mixtures containing ethylenediamine) is very effective in reducing aromatic ring systems to monoalkenes. In this respect, it resembles the chemistry of lithium dissolved in low-molecular-weight amines. Furthermore, in the presence of a proton source like *t*-butyl alcohol, calcium reductions (like lithium) can be stopped at the dihydro stage to give Birch-type products. We have now found that the calcium reagent is very effective in reducing epoxides to alcohols. Like lithium in ethylenediamine, the calcium system can effect facile reductions of labile epoxides. Thus, 9,10-epoxytetrahydronaphthalene can be reduced by calcium to *trans*-9-decalol (88% yield), *exo*-2,3-epoxynorbornane to *exo*-2-bornanol (90%), l-methylepoxycylohexane to l-methylcyclohexanol (94%), and 1,2-epoxyhexane to 2-hexanol (91%). These results are quite comparable to the reduction of these same epoxides by lithium, but the calcium procedure would be the method of choice in large-scale reductions where costs and safety become significant factors. The calcium-amine reducing agent can also be used to effect ring reduction of methylated aromatic carboxylic acids. In the cases studied thus far, dihydro products seem to predominate. This is an interesting result since the only proton source in these cases is the solvent, ethylenediamine.

## Rensselaer Polytechnic Institute
## Troy, New York 12181

### *321. Selective Transformations of Carbonyl Ligands to Organic Molecules*

*A.R. Cutler* **$100,000**
*Department of Chemistry*

Methoxyacetyl complexes M–$COCH_2OCH_3$ have been isomerized selectively to M–$CH_2CO_2CH_3$ and to M–$CH(OCH_3)CHO$ complexes and have been reduced to M–$CH_2CHO$ [M = Cp(CO)(L)Fe; L = CO,$PPh_3$,$P(OCH_3)_3$]. The ligand reactions involved in converting the methoxyacetyl template into the $C_2$ organics $CH_3CO_2CH_3$, $CH_2(OCH_3)CHO$, and $CH_3CHO$ (respectively) thus have been established, and the unique roles of ligated ketene [$M^+$–($\eta^2$-$CH_2$=C=O)] and the hydride migration reaction, M–$C(OCH_3)CH_2OR^+$ to M–$[CH(OCH_3)=CHOR]^+$, have been demonstrated. Carbonylation studies of $Cp(CO)_2FeCH_2R$ [in which Cp was replaced successively by $\eta^5$-indenyl, –$C_5Me_5$, Fe by Ru, CO by $PPh_3$, and $P(OMe)_3$, and R = H, $CH_3$, Ph, OMe, $CO_2Me$] and or $L(CO)_3Co$–R and $L_2(CO)_2Co$–R [L = $PPh_3$,$PMePh_2$; R = $CH_2OMe$, $CH_2CO_2Me$] provided mild conditions (1 atm CO) for generating acyl ligands. Synthetic and labeling studies have elaborated further on the role of the "indenyl effect", $\eta^5$ / $\eta^3$-indenyl ring slippage, in the carbonylation chemistry of ($\eta^5$-In)(CO)(L)Fe–R.

## University of Rochester
## Rochester, New York 14627

### *322. Transition Metal Activation and Functionalization of Carbon Hydrogen Bonds*

*W.D. Jones* **$143,000**
*Department of Chemistry* **(18 mo.)**

This project focuses on the activation and cleavage of carbon–hydrogen bonds by homogeneous transition metal compounds. Our initial work has been directed towards understanding the kinetic vs. thermodynamic differences between alkane and arene activation by the reactive intermediate [$(C_5Me_5)Rh(PMe_3)$]. We have found a tremendous thermodynamic preference for arene activation, whereas the kinetic preference of the intermediate is extremely small. Other studies involve the mechanism and thermodynamics of intra- and intermolecular alkane and arene C–H bond activation in the series of complexes $(C_5Me_5)Rh(PMe_2R)(R)(H)$. For R = propyl or benzyl there is little kinetic selectivity for intra- vs. intermolecular activation of arenes or alkanes, although there is a large thermodynamic selectivity favoring intramolecular activation. Temperature-dependent rate studies indicate that differences in the entropy of activation between intra- and intermolecular reaction are not important in this system.

## University of South Carolina
## Columbia, South Carolina 29208

### *323. Studies of the Hydrogenation of Small Unsaturated Molecules Using Organometallic Cluster Compounds as Catalysts*

*R.D. Adams* **$103,000**
*Department of Chemistry*

Polynuclear transition metal (cluster) compounds are being investigated for their ability: (1) to activate hydrogen and unsaturated small molecules (e.g., CO, $CO_2$, alkynes, alkenes, and related heteronuclear molecules); (2) to induce bonding rearrangements in ligands; and (3) to produce hydrogen addition to unsaturated ligands. The products of reaction sequences are isolated and characterized by infrared, NMR, and single-crystal x-ray diffraction methods. The importance of polynuclear coordination in ligand transformations is studied. It is hoped that the reaction sequences can be converted into useful catalytic cycles.

## SRI International
## Menlo Park, California 94025

### *324. High-Temperature Chemistry of Complex Vaporization-Decomposition Processes*

*D.L. Hildenbrand,* **$67,300**
*R.D. Brittain, K.H. Lau*
*Physical Sciences Division*

The project objective is to obtain fundamental thermodynamic data for a variety of high-temperature vaporization-decomposition processes that are relevant to current and emerging energy technologies such as stack gas cleanup, coal gasification, hydrogen generation, and MHD. These processes are being studied by high-temperature mass spectrometry and the torsion-effusion method so that both vapor composition and absolute pressures are determined. For substances that simultaneously undergo both decomposition and direct vaporization, particular emphasis is on quantitative determination of the relative contributions from each process, and on thermochemical characterization of the complex vapor species. Current studies are concerned with nickel and cobalt sulfates and with the alkali chromates. The chromates are especially interesting in that vaporization occurs mainly via stable gaseous metal chromate molecules, about which little is known. The effects of certain additives that catalyze sulfate decomposition are also being studied, since kinetic and mechanistic features have a crucial bearing on the interpretation of the dynamic effusion measurements, as well as on the technological applications of these processes.

## Stanford University
## Stanford, California 94305

### *325. Catalytic Steam Gasification of Carbon*

*M. Boudart* **$75,000**
*Department of Chemical Engineering*

Extensive investigations of the last decade have improved understanding of the bonding and the electronic properties of transition metal carbides. Temperature-programmed reaction between $MoO_3$ or $WO_3$ with $NH_3$ provides a new way to prepare $Mo_2N$ and $W_2N$ powders with specific surface areas as high as 220 and 100 $m^2g^{-1}$, respectively. Temperature-programmed carburization of $Mo_2N$ and $W_2N$ powders in $CH_4$–$H_2$ mixtures leads to metastable face-centered cubic carbide phases. The high specific surface area of $Mo_2C$ or $W_2C$, based on the BET method or methods recommended for assessing the specific surface area of microporous materials, is higher than ever previously reported. In discussing the surface reactivity and catalytic activity of carbides, the surface composition should be known. The importance of surface composition was underscored by studies that showed that the steady-state rate of ammonia synthesis on various molybdenum powders is reached only after the surface has taken up nitrogen-forming $\gamma$-$Mo_2N$, the stable phase during ammonia synthesis. Investigations into the surface composition of tungsten carbide samples have been examined by Auger electron spectroscopy and electron spin resonance. Deviations from stoichiometry involve excess carbon in the form of polymeric ("graphitic") overlayers, oxygen, and excess tungsten or molybdenum metal that is carbon deficient.

### *326. Molecular Beam Studies of the Dynamics and Kinetics of Heterogeneous Reactions on Single-Crystal Surfaces*

*R.J. Madix* **$120,000**
*Department of Chemical Engineering*

The dynamics of reactive processes with single-crystal nickel surfaces have been studied using molecular beam scattering techniques in combination with ultrahigh vacuum surface science methods. The nature of the precursor state for associative chemisorption has been examined for a classical prototype, CO on Ni(100). On the clean surface there is no reversibly bound precursor, and the chemisorption probability is governed by trapping at the surface. The small fraction of the molecules that reflect from the surface without chemisorption are quasi-elastically scattered, not trapped, even at the lowest kinetic energies of the beam employed. On the surface saturated with adsorbed CO, trapping into a precursor state is strongly dependent on the incident energy of the molecules. At low kinetic energies trapping into a weakly bound state dominates the scattering, and at these energies adsorption can qualitatively be described by the classical precursor models. At high kinetic energy, however, molecules scatter elastically from the adsorbed CO, and adsorption is Langmuirian. This novel result recasts the fundamental viewpoint of adsorption kinetics. In a second study on this surface we examined the dependence of the activation of alkanes on translational energy, and vibrational energy to some extent. For the alkanes, $C_1$ to $C_4$, no measurable reaction occurred for translational energies below 10 kJ/mol at any surface temperature studied. Above this energy the activation probabilities increased to values above 0.1, showing progressively weaker dependence on kinetic energy with increasing molecular weight. Angular distributions of the scattered hydrocarbons below the activation threshold indicated a stronger interaction of the higher molecular weight species with the surface. The results are interpreted in terms of dissipative channels that drain off energy from the reaction coordinate in the larger alkanes.

## Syracuse University
## Syracuse, New York 13210

### *327. Metal–Support Interactions: The Effect of Catalyst Preparation on Catalytic Activity*

*J.A. Schwarz* **$84,300**
*Department of Chemical Engineering and Materials Science*

A scientific basis for design of catalysts can be developed by examining the relationship between catalyst preparation procedures and the dispersion, activity, and selectivity of the finished catalyst. In our studies, the master variable for preparation of catalysts is the pH of the solution. Nickel catalysts dispersed on a $\gamma$-$Al_2O_3$ carrier were prepared using nickel nitrate by wet and incipient wetness procedures. The following techniques were used to characterize each of the catalysts: (1) temperature-programmed desorption (TPD), (2) temperature-programmed reaction (TPR), (3) steady-state kinetics, and (4) temperature-programmed surface reaction (TPSR). The method of preparation strongly affects the dispersion of the catalyst, defined as the ratio of nickel that can desorb hydrogen during TPD to the total nickel loading. The dispersion of catalysts prepared by wet impregnation shows an inverse relationship with weight loading. Wet impregnation procedures provide design equations, which allows for quantitative determination of catalyst activity, selectivity, and carbon deposition. These equations are solely dependent on the solution phase parameters: nickel nitrate concentration, pH, and ionic strength of the electrolyte. The dispersion of catalysts prepared by incipient wetness procedures also shows an inverse relation with increased weight loading but the dispersion depends on the initial pH of the solution, increasing with decreasing pH. The activity, selectivity, and carbon deposition on these catalysts are, likewise, a function of the pH of the impregnant.

## University of Texas
## Austin, Texas 78712

### *328. Study of Synthesis Gas Conversion over Metal Oxides*

*J.G. Ekerdt* **$59,000**
*Department of Chemical Engineering*

The goals of this project are (1) identification of the reaction intermediates present during CO hydrogenation reactions, (2) determination of the reaction pathways whereby the intermediates are converted into products, and (3) the development of an understanding of the causes for catalytic activity and selectivity to $C_{2+}$ products. Direct CO hydrogenation into branched hydrocarbons, isosynthesis, and into low-weight alcohols is investigated over zirconium dioxide-based catalysts. Experiments are conducted at 35 atm and at atmospheric pressure. Oxygen and carbon isotope-labelling studies and reaction-rate studies at both pressures have revealed the reactions that occur during chain growth and termination, and during the activation of CO to the intermediates needed in chain growth. The studies also suggest the configuration of the active site at the zirconium dioxide surface. The effect of alkali additives on the concentration of active sites and on the rate of termination to branched products, and how catalyst synthesis conditions affect the concentration of the sites for CO activation are currently under investigation.

### 329. Morphological Aspects of Surface Reactions

*J.M. White* **$107,000**
*Department of Chemistry*

An integrated research project combining reaction rate, surface spectroscopy, and surface microscopy will be conducted on rhodium-based catalysts including atomically dispersed, small clusters and thin films supported on oxides and bulk single crystals. Reactions under investigation include $H_2$–$D_2$ exchange, carbon monoxide oxidation, and hydrogenation of ethylene. Rate measurements will be made from pressures as low as $10^{-6}$ to 760 Torr and at temperatures below 350 K. Detailed surface analysis will be made using thermal desorption spectroscopy, secondary ion mass spectrometry, vibrational spectroscopy, and photoemission. Electron microscopy will be performed to provide particle size and morphology. The sample environments will be carefully controlled and evaluated, particularly during transfers between various instruments. The combination of this data on a series of closely controlled samples will provide for direct correlations between particle morphology and catalytic activity over a broad range of conditions.

## Texas A and M University
College Station, Texas 77843

### 330. Catalysts and Mechanisms in Synthesis Reactions

*J.H. Lunsford* **$90,100**
*Department of Chemistry*

This project seeks to understand the support and promoter effects that influence the catalytic properties of supported metals (e.g., palladium) for the formation of alcohols. Controlled modification of palladium supported on silica, for example by the addition of lithium ions, can transform an inactive catalyst into one that rivals commercial catalysts for methanol synthesis activity. Pure palladium is relatively inactive, thus the support plays an essential role perhaps by stabilizing intermediate species. Infrared experiments are under way to detect these intermediates if they exist. Another aspect of the research involves a study of matrix-isolated gas-phase radicals that are produced on surfaces of catalytic importance. Recent work on lithium-promoted magnesium oxide shows that surface $[Li^+O^-]$ centers are active in the generation of methyl radicals from methane. Radical formation has been compared over bismuth oxide, bismuth molybdate, lead oxide, magnesium oxide, and lithium-promoted magnesium oxide with methane, ethane, ethylene, and propylene as the reactants. All of the oxides were capable of generating alkyl radicals from propylene, which has the smallest C–H bond strength, but only MgO and Li–MgO were capable of generating alkyl radicals from alkanes. Additional studies have shown that several of the rare-earth oxides ($La_2O_3$, $Nd_2O_3$, and $Dy_2O_3$) are also effective for generating gas-phase methyl radicals from methane.

### 331. Properties of Lanthanide Oxides as Supports for Transition Metal Catalysts

*M.P. Rosynek* **$76,500**
*Department of Chemistry*

This project is an investigation of the influence exerted by lanthanide oxide support materials on the structure, reactivity, and chemical nature of hydrogen-containing surface carbon deposited on dispersed transition metal catalysts. Initial studies have focused primarily on catalyst preparation and characterization, with particular emphasis on the application of temperature-programmed reduction (TPR) techniques. We have examined the reduction behaviors of dispersed cobalt, nickel, and rhodium catalysts, prepared from chloride, nitrate, and chloramine precursors. Using a combination of TPR/MS and XPS techniques, we have demonstrated that both the mechanism of the reduction process and the nature of the resulting surface for cobalt catalysts supported on $SiO_2$, $TiO_2$, $La_2O_3$, and $Eu_2O_3$ are strongly dependent on whether a preoxidation step is employed in the pretreatment sequence. Direct reduction in $H_2$ of supported $Co(NO_3)_2$ results in a catalyst containing surface regions of virtually irreducible Co(II), while preoxidation of the nitrate to $Co_3O_4$ prior to $H_2$ treatment facilitates complete reduction to metallic cobalt. The TPR method has also revealed that rhodium salts are considerably more difficult to reduce when dispersed on basic oxides such as $La_2O_3$ and $Eu_2O_3$ than on neutral materials such as $SiO_2$.

## University of Utah
Salt Lake City, Utah 84112

### 332. Ligand Intermediates in Metal-Catalyzed CO Reduction

*J.A. Gladysz* **$100,600**
*Department of Chemistry*

The project objective is the synthesis and study of homogeneous complexes containing ligand types (-CHO, =CHOH, $-CH_2OH$, ≡C, ≡CH, $=CH_2$, $H_2C=O$, -OCHO, $CO_2$, and so forth) believed to be intermediate in the metal-catalyzed conversion of $CO/H_2$ and $CO_2/H_2$ gas mixtures to organic molecules. Mechanistic understanding of the steps involved in catalytic CO and $CO_2$ reduction, and insight needed for the design of new catalysts are sought. We have just completed a study of the synthesis and reactivity of $\alpha$-hydroxyalkyl complexes $L_nMCH(R)OH$. The first isolable complex of this type to undergo carbonylation (to an acyl complex $L_nMCOCH(R)OH$) has been discovered. Intramolecular hydrogen bonding has been shown to facilitate this conversion. Sequential treatment of formyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ with LDA and then $CH_3OSO_2CF_3$ gives $(\eta^5\text{-}C_5H_4CHO)Re(NO)(PPh_3)(CH_3)$. This is the first carbon–carbon bond-forming reaction of an $\eta^1$-formyl ligand, and we have completed a detailed mechanistic study. We find that the reaction of hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ with *n*-BuLi/TMEDA to give $Li^+$ $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ proceeds via $(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(H)$: a new "ligand-assisted" metal hydride deprotonation mechanism. This intramolecular rearrangement is accelerated 10,000-fold (-92 °C) when $Li^+$ is substituted by $K^+$, and mechanistic studies are continuing.

### 333. Liquid and Solid $^{13}C$ Magnetic Resonance Study of Hydrocarbons and Related Substances

*D.M. Grant, R.J. Pugmire* **$100,200**
*Department of Chemistry*

We recently finished our work on hydroaromatic model compounds, which showed a correlation between conformation and chemical shifts. Work on solid-state nuclear magnetic resonance (NMR) methods of single-crystal and magic angle spinning (MAS) involves model compounds to be used for calibration and standardization of spectra of coals, coal macerals, and so forth. Current work on single crystals provides a better understanding of shielding anisotropies and the orientational features of the important dipolar dephasing experiment. Rotating a single crystal gives data on chemical shift anisotropy; initial results show relaxation anisotropy can be studied. Both the dipolar dephasing rate and relaxation anisotropy depend on the orientation of C–H bonds. The single-crystal work provides basic information on these processes. An ultrahigh-speed (0 to 8,000 r.p.s.) rotor for MAS work has been developed. The higher rotation rates allow use of our 4.7 tesla magnet instead of the 2.35 tesla systems used previously. Reduced rotor diameters also allow for significant increases in the RF fields at reduced power dissipation and improved cross-polarization (CP) efficiencies. Work on the molecular dynamics of benzyl alcohol and pentanol adsorbed on zeolites using CP/MAS methods contributes information on catalytic processes.

### 334. *Comprehensive Characterization Studies of Sulfided Molybdena Catalysts*

*F.E. Massoth* **$72,100**
*Department of Fuels Engineering*

The goal of the present work is to characterize a wide variety of supported molybdena sulfide catalysts with a number of different characterization techniques, and determine their catalytic activities for model compounds representative of several functionalities present on these catalysts in order to relate catalytic activities to catalyst properties (structure, dispersion, active sites) of the active phase. Several newer techniques not available or not used in earlier studies, as well as some conventional ones, will be used to characterize the catalysts. These include chemisorption of selected gases, active OH content of the supports, $H_2{}^{35}S$ exchange, electron spectroscopy for chemical analysis, x-ray diffraction, and SH content. A number of catalysts containing 4 or 8% molybdenum on different aluminas, prepared by impregnation at various pH, have widely different hydrodesulfurization activities. Detailed characterization of these catalysts is in progress.

## Wayne State University
## Detroit, Michigan 48202

### 335. *Surface Composition–Reactivity Relationships in Heterogeneous Catalysis*

*A. Brenner* **$87,000**
*Department of Chemistry*

This group recently found that the activity of metal/alumina catalysts for benzene hydrogenation can strongly depend on the temperature of activation. To understand this synthesis-activity relationship, temperature-programmed reduction and oxidation studies at temperatures up to 1200°C have been done. Results have been compared to the redox behavior of the bulk powders. These studies delineate the temperatures required for reduction and reoxidation. This is the first time that a substantial series of catalysts has been studied by a single group using a standard set of conditions. It was found that the oxides of the noble metals, $RuO_2$, $Re_2O_7$, and $Rh_2O_3$, are easy to reduce; the oxides $Fe_2O_3$, $MoO_3$, $WO_3$, CoO, NiO, and the salt $H_2OsCl_6$ can only be completely reduced at temperatures near 1000°C; and the oxides $Cr_2O_3$, $Mn_2O_3$, $V_2O_5$, $ThO_2$, and $UO_3$ can not be fully reduced under our reaction conditions. The kinetic reducibility of these materials correlates with their thermodynamic reducibility. $H_2$–$D_2$ exchange over molybdenum supported on $Al_2O_3$ and $SiO_2$ has been studied. The complex $Mo(CO)_6$ as well as the subcarbonyl $Mo(CO)_3$ are inactive, as expected for a molecular species with limited bonding sites. As the amount of residual CO falls below 1 CO/Mo, indicating the formation of some bare metal, the rate of reaction dramatically increases. The formal turnover frequency (turnovers per total metal in a catalyst) of molybdenum supported on alumina and silica is 0.2 $s^{-1}$ at 77 K. Over bulk molybdenum the activity is about 100-fold less, indicating that the support modifies the active site. Surface OH also participates in the reaction.

## University of Wisconsin
## Madison, Wisconsin 53706

### 336. *Organometallic Chemistry of Bimetallic Compounds*

*C.P. Casey* **$63,000**
*Department of Chemistry* **(7 mo.)**

The organometallic chemistry of bimetallic compounds will be investigated (1) to discover new heterobimetallic compounds that can serve as catalysts for CO hydrogenation and (2) to obtain a better understanding of the chemistry of bridging hydrocarbon ligands bonded to multiple metal centers. Heterobimetallic compounds in which the metals are linked by a heterodifunctional ligand and by a metal–metal bond will be synthesized. A search will be made for such compounds that will react with $H_2$ to produce heterobimetallic dihydrides. 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 chemistry of newly discovered bridging methylidyne complexes will be studied as models for surface bound CH units. Reactions of methylidyne complexes with water, bases, CO, and alkenes will be explored. The synthesis and reactions of bimetallic compounds with a bridging methylene and terminal methyl group will be studied as models for the carbon–carbon bond-forming process in the Fischer Tropsch reaction.

### 337. *Acid Sites Formed by Doping Cations onto Oxide Surfaces: Theoretical Aspects and Experimental Studies*

*J.A. Dumesic* **$66,700**
*Department of Chemical Engineering*

Our studies focus on three aspects of the acidic properties of acid sites formed by doping metal cations onto oxide supports. In studies of iron cations supported on various oxides, we have determined (1) the coordination of the iron cations, using Mossbauer spectroscopy; and (2) the number and nature of the acid sites, using gravimetric measurements and infrared spectroscopy of adsorbed pyridine. The coordination of the iron cations on the supports was found qualitatively to increase in the order: $SiO_2 < TiO_2 < Al_2O_3 < MgO$. Our studies of different dopants on silica indicated that scandium, magnesium, iron, tin, aluminum, and gallium all generated Lewis acidity, and the frequency of the 19b infrared band of adsorbed pyridine was observed to shift to higher wave number in the above order of these respective cations on silica. Studies of the desorption of pyridine at elevated temperatures indicated that increasing infrared frequency corresponded to stronger bonding of pyridine. Microcalorimetric measurements were made of the heat of pyridine adsorption on silica-supported aluminum, iron, and MgO and on blank silica; and the following values of the heats at low pyridine coverages were determined on these respective samples: 220, 200, 140, and 90 kJ/mol. These values indicate that the Lewis acid strength can be varied by changing the dopant cation.

## Yale University
## New Haven, Connecticut 06511

### *338. Studies in Carbon–Carbon Bond Activation*
*R.H. Crabtree* **$99,000**
*Department of Chemistry*

The aim of this research is to find ways of cleaving carbon–carbon bonds in alkanes and other related hydrocarbons with transition metal complexes. We believe that to do this we first have to break carbon–hydrogen bonds to give an organometallic species that can subsequently undergo a carbon–carbon bond cleavage. For example, we had shown that cyclopentanes can be dehydrogenated to cyclopentadienyl complexes by $[IrH_2(solv)_2L_2]$ cations. We have now shown that a similar reaction with *gem*-dimethylcyclopentane gives a dimethylcyclopentadiene complex. This undergoes alkyl transfer to give a methyl iridium cyclopentadienyl complex. This is the first case of homogeneous carbon–carbon bond cleavage in alkanes by a metal complex. Initial studies suggest that a second mechanism is operating that might be applicable to alkanes in general. We feel that we may be close to having a homogeneous reforming catalyst.

### *339. Selectivity, Activity, and Metal–Support Interactions of Rhodium Bimetallic Catalysts*
*G.L. Haller* **$89,900**
*Department of Chemical Engineering*

Three bimetallic systems have been studied: Rh–Ag, Ru–Cu, and Rh–Pt, to determine the effect of support on the kind and degree of metal–metal interaction. EXAFS analysis indicates that there is greater Rh–Ag interaction when this bimetallic is supported on $TiO_2$ than on $SiO_2$. These metals, which are immiscible in the bulk, form nearly homogeneous bimetallic small clusters on $TiO_2$ support. Using catalytic probes, we have determined a similar structure for Ru–Cu clusters on Cab-O-Sil HS5 silica, but there is less Ru–Cu interaction on all other silicas investigated. Hydrogen spillover occurs on the morphology that results in the latter systems, but both hydrogen chemisorption and spillover are suppressed by the more homogeneous morphology of Ru–Cu clusters on HS5 silica. Bimetallic clusters of Rh–Pt supported on $TiO_2$ are surface enriched in rhodium and behave as if they consisted of pure rhodium up to 60% overall mole fraction of rhodium in the bimetallic clusters. The metal–oxide interaction between rhodium or platinum and $TiO_2$ is quantitatively different. This strong metal–support interaction (SMSI) is easily reversed by the products of reaction of CO hydrogenation on $Rh/TiO_2$ but only slowly reversed on $Pt/TiO_2$. The stoichiometric consumption of the reaction that breaks the metal–oxide interaction is about one oxygen atom per surface rhodium atom but nearly two oxygen atoms per surface platinum atom.

### *340. The Role of d-Electrons in Chemisorption and Metal–Support Interactions Studied by Electron Spectroscopy*
*V.E. Henrich* **$69,900**
*Section of Applied Physics*

The nature of the interaction between small metal catalyst particles and transition-metal-oxide supports that occurs in strong metal–support interactions (SMSI) is being investigated by using model catalysts consisting of rhodium deposited onto single-crystal rutile $TiO_2$ supports in UHV. Surface-sensitive electron spectroscopies (UPS, XPS, Auger, EELS, and so forth) are used to study the electronic and geometric properties of the model catalysts and their chemisorption properties for various processing conditions. The use of model catalysts permits the (at least partial) separation of geometric and electronic contributions to catalyst behavior. Previous measurements showed that oxide species migrate onto catalyst particles during high-temperature reduction, blocking chemisorption sites. Prereduction chemisorption behavior could be restored by simply mechanically removing the oxide moieties by sputtering. Recent photoemission measurements of the valence band structure of the metal–support system show that electronic charge is transferred from the $Ti^{3+}$ cations of reduced support surfaces to the catalyst particles even in the absence of oxide migration. This charge transfer, although significant for small metal particles, does not alter the chemisorption properties of the catalyst, and thus does not appear to contribute to the change in properties exhibited by catalysts in the SMSI state.

### *341. Energies of Organic Compounds*
*K.B. Wiberg* **$97,000**
*Department of Chemistry*

This research project is designed to provide information on the energies of organic compounds via reaction calorimetry and theoretical calculations, and to use these data to improve empirical and semiempirical schemes for estimating the energies of these compounds. Heats of vaporization are being measured so that the thermochemical data may be corrected to the vapor phase. The data are also being used to explore steric effects and other structural effects on energies. Reactions being studied include the hydration of alkenes, hydrolysis of ketals, reduction of ketones, and rearrangements of small-ring hydrocarbons. Theoretical calculations are used to estimate the energies of interesting compounds, which have not as yet been prepared, and to study the intramolecular interactions (force constants and rotational barriers) and charge distributions that are used in molecular mechanics.

# Separations and Analysis

## Aerospace Corporation
## Los Angeles, California 90009

### *342. Isotopically Selective, Two-Step, Laser Photodissociation of Molecules*
*P.F. Zittel*
*Chemistry and Physics Laboratory*

This research project is directed toward understanding photophysical, energy transfer, and chemical processes relevant to isotope separation by two-step laser photodissociation of small molecules. 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 scavenging of the photofragments. Infrared laser absorption measurements and mass spectrometric analysis of the photoproducts reveal the effect of vibrational excitation on the photodissociation cross section and give the isotope enrichments. Of particular interest are measurements of vibrationally state-specific photodissociation cross sections for different vibrational modes of a molecule. Two-step photodissociation of OCS has led to the separation of all stable isotopes of oxygen, carbon, and sulfur, and to a determination of the 249 nm photodissociation cross section of the $\nu_1$ and $2\nu_2$ vibrational states of OCS. These results are combined with temperature-dependent photoabsorption spectra to obtain photodissociation cross sections for the vibrationless and $\nu_2$ vibrational states of OCS. A frequency-doubled $CO_2$ laser is currently being used to access the $\nu_3$ vibrational state. Previous work on gas-phase, room-temperature samples is also being extended to cryogenic solutions.

## University of Arizona
## Tucson, Arizona 85721

### 343. *Chelating Extractants of Improved Selectivity*

*H. Freiser* **$80,000**
*Department of Chemistry*

This research is designed to develop chelating extractants of improved selectivity for separating individual lanthanide and actinide ions. Emphasis is on uncovering molecular structural parameters of importance in the design of such extractants. Use of pattern recognition techniques is one approach to the elucidation of molecular parameters. Study of the extraction equilibria for representative tervalent lanthanides with selected members of chelating extractants of the N-acylphenylhydroxylamine, 8-quinolinol, acylpyrazolone, and other families is being used, because they include some likely candidate extractants and because present gaps in fundamental data required to apply pattern recognition are thereby being eliminated.

## Auburn University
## Auburn, Alabama 36849

### 344. *Interfacial Chemistry in Solvent Extraction Systems*

*R.D. Neuman* **$97,500**
*Department of Chemical Engineering*

We earlier proposed that aggregates, possibly reversed micelles, form above a critical HDEHP concentration in the system di(2-ethylhexyl) phosphoric acid (HDEHP)/n-hexane/$CaCl_2$ solution, and their formation corresponds to significant increases in both the amount and rate of metal extraction. Reversed micellar catalysis is believed to be responsible for the enhancement of the extraction process. Work is in progress to determine whether this phenomenon is general to organophosphorous extractants, by investigating the interfacial tension, equilibrium distribution and extraction kinetics behavior of different extractants (HDEHP and PC 88A), diluents (n-hexane and benzene), and metal ions ($Ca^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$, and $Zn^{2+}$). Emphasis is also given to the nature, size, and size distribution of aggregates in organic diluents, using a variety of techniques such as vapor-pressure osmometry, proton magnetic resonance, intensity and quasi-elastic light scattering, and Karl Fischer titration. The interaction of model long-chain phosphate extractants with metal ions will be examined employing a Brooks' frame for monomolecular film studies at liquid–liquid interfaces. Further development of an advanced laser heterodyne light-scattering apparatus will permit determination of the viscoelastic properties of extractants at the liquid/liquid interface of solvent extraction systems.

## Brigham Young University
## Provo, Utah 84602

### 345. *Novel Macrocyclic Carriers for Proton-Coupled Liquid Membrane Transport*

*J.D. Lamb* **$75,000**
*Department of Chemistry*

We investigate macrocycle-mediated metal cation transport in hydrophobic liquid membrane systems of the bulk, emulsion, and supported types with the objective of separating cations. Research involves design, synthesis, and characterization of new, acidic macrocyclic carriers that permit the coupling of cation transport to the reverse flux of protons from an acidic receiving phase. Macrocycles of several basic designs are pursued, including pyridono-, triazolo-, phosphono-, and sulfonamide-based structures; the common feature is that the acidic group is part of the principal ring structure. Bulk membrane experiments have shown that several of these ligands have excellent flux and selectivity characteristics; these ligands are investigated further by $pK_a$ and cation binding constant measurements. A second area of emphasis is the incorporation of macrocyclic carriers into liquid membrances supported on porous polymer films. The effects of solvent and ligand partitioning between membrane and water phases are critical factors. The effect of specific ligand structural variations on these factors is being determined.

## Brown University
## Providence, Rhode Island 02912

### 346. *Photochemical Generation of the Optoacoustic Effect*

*G.J. Diebold* **$65,000**
*Department of Chemistry*

Experiments are carried out to determine the properties of the inverse optoacoustic effect. We have found that sound generation arises from emission of blackbody radiation from the cell walls, and that modulation of the radiation density in the cell is responsible for sound production. We have constructed a model for the inverse optoacoustic effect that accounts for the temperature, phase, and frequency dependence of the effect. An anomalous signal dependence on the concentration of infrared active species was found. Experimental and theoretical work is conducted to explain these results and to determine the influence of heat conduction on signal generation. For highly absorbing species, such as $SF_6$, heat conduction effects and the coupling between the thermal and acoustic waves become important in the generation of optoacoustic signals. In the limit where all of the absorption occurs over a short distance compared with the thermal diffusion length of the gas, a piston model can be used to explain the optoacoustic signal amplitude.

## University of California
## Los Angeles, California 90024

### *347. Multiheteromacrocycles That Complex Metal Ions*
*D.J. Cram* **$120,300**
*Department of Chemistry and Biochemistry*

The general objectives of this research are to design, synthesize, and evaluate new types of cyclic and polycyclic organic ligand systems for their abilities to complex and lipophilize selectively guest metal ions. Correlations are sought between ligand structures and their binding free energies, their rates of complexation-decomplexation, and their solvation effects. Desired properties are high selectivity, rapid rates of complexation, and incorporation of detecting systems into the ligand. The principles of complementarity of host and guest and of host preorganization are being tested as guides in ligand design. Organized arrays of most of the functional groups of organic chemistry are being tested as ligating sites. Particular emphasis is placed on those systems that contain weakly basic nitrogen, sulfur in various oxidation states, and carbonyl groups of various types. Synthetic methods are being developed that lead to enforced preorganization of binding sites. Solvent effects on binding are being studied.

## Colorado State University
## Fort Collins, Colorado 80523

### *348. Study of Improved Methods for Predicting Chemical Equilibria*
*T.G. Lenz* **$122,000**
*Department of Agriculture and Chemical Engineering* **(18 mo.)**

The project objective is to develop improved techniques for predicting condensed-phase chemical equilibria. Studies emphasize polycyclic heteroatom compounds that have significant steric and strain effects. Specific experimental studies will clearly delineate intramolecular bond strain and substituent rotational and vibrational contributions to reaction $\Delta H^\circ$ and $\Delta S^\circ$, using substituted anthracenes and maleic anhydrides at dilute concentrations in a variety of solvents. Experimental results will be used in developing and testing a modified force-field model for calculating thermodynamic functions for reactant and product molecules. The full computational model will incorporate UNIFAC techniques for estimating activity coefficients. Both the force-field model for estimating gas phase thermochemical properties and the UNIFAC solution activity coefficient model have separately proven reliable and generally applicable. The force-field techniques, important in chemistry but used very little to date by chemical engineers, are thus coupled with the UNIFAC model to give a potentially powerful tool for predicting condensed-phase chemical equilibria for a wide variety of reactions of practical interest.

## Columbia University
## New York, New York 10027

### *349. Utilization of Magnetic Effects as a Means of Isotope Enrichment*
*N.J. Turro* **$78,000**
*Department of Chemistry*

This research is aimed at developing novel methods for the separation of isotopes based on exploitation of differences in magnetic properties of isotopes. Emphasis has been placed on discovering reactions and conditions that allow the separation of isotopes that possess a finite magnetic moment from those that do not possess a magnetic moment. Successful systems have been designed for separation of $^{13}C$ (a magnetic isotope) from $^{12}C$ (a nonmagnetic isotope), and for the separation of $^{17}O$ (a magnetic isotope) from $^{16}O$ and $^{18}O$ (nonmagnetic isotopes). The restricted space provided by porous silica has proven to be an excellent environment for efficient separation of $^{13}C$ and $^{12}C$ based on the photolysis of dibenzyl ketone. The porous internal structure of zeolites is also an excellent environment for $^{13}C$ enrichment. The variation in zeolite structure offers a range of environments to serve for $^{13}C$ enrichment. Experiments are now in progress to determine how to optimize $^{13}C$ enrichment on zeolites.

## University of Delaware
## Newark, Delaware 19716

### *350. Studies of the Analyte–Carrier Interface in Multicomponent Flow Injection Analysis*
*S.D. Brown* **$60,600**
*Department of Chemistry*

The use of flowing streams to transport injected analytes has received considerable attention lately. Situations where the injected analyte reacts with reagents present in the carrier stream have received almost no study. This project involves the study of product distributions with an injected bolus. Initial studies have focused on the characterization of the flow reactor and on the development of software for the analysis of mixtures and for the study of reaction kinetics. These studies will be useful in analyses of the distribution of reaction products across the interface of the injected bolus and the carrier stream in flow injection analyses.

## George Washington University
## Washington, District of Columbia 20052

### *351. New High-Temperature Plasmas and Sample Introduction Systems for Analytical Atomic Emission Spectrometry*
*A. Montaser* **$55,300**
*Department of Chemistry*

New high-temperature plasmas and new sample introduction systems are developed for rapid elemental analysis of solutions and solids using atomic emission spectrometry. These devices offer promise of solving singularly difficult analytical problems that exist now or are likely to arise in the future in the various fields of energy generation, environmental pollution, biomedicine, and nutrition. Emphasis is placed on: (1) generation and fundamental investigation of annular helium inductively coupled plasmas suitable for the excitation of high-energy spectral lines, to enhance the detecting powers for a number of elements; (2) generation of plasmas that require low gas flows and low input power, to decrease the cost of analytical determination; and (3) 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.

## Georgetown University
## Washington, District of Columbia 20057

### 352. *Study of the Performance of a New Detector Class for Liquid Chromatography*

*G. Guiochon* **$72,200**
*Department of Chemistry*

We will study a new class of detectors for liquid chromatography. The general principle of these detectors uses nebulization of the column effluent in a stream of tepid gas where the solvent is vaporized. The nonvolatile solutes form small particles that are carried by the gas stream across an intense light beam. Light scattered by the particles is a function of their size (i.e., of the concentration of nonvolatile solutes in the column effluent). The research involves studies on the nebulization of the column effluent (comparison among results obtained with a concentric nebulizer, an ultrasonic nozzle, and a pierced diaphragm), on the light scattering (influence of the light beam energy and wavelength), and on the acquisition mode of the signal (continuous beam versus pulsed beam with a box-car amplifier). We will also investigate alternative methods to detect the solutes by separating particles of nonvolatile material from the stream of gas and vapor.

## University of Georgia
## Athens, Georgia 30602

### 353. *Fundamental Studies of Separation Processes*

*L.B. Rogers* **$65,400**
*Department of Chemistry*

There are three major areas of effort in this research. The first is concerned with the fundamental aspects of two different forms of liquid chromatography, adsorption, and steric exclusion, especially with respect to interaction during a given separation. Nonporphyrin compounds of vanadium and nickel, and commercial mixtures of oligomers of polystyrene are ideal solutes for these studies because each type of sample covers a wide range of molecular weights. The second area involves the identification of those nonporphyrin compounds using a variety of techniques. The third area is concerned with recycle chromatography, a promising approach to separations of isotopic species.

## Georgia Institute of Technology
## Atlanta, Georgia 30332

### 354. *Fundamental Studies with a Monodisperse Aerosol-Based Liquid Chromatography/Mass Spectrometry Interface (MAGIC-LC/MS)*

*R.F. Browner* **$132,000**
*Department of Chemistry* **(24 mo.)**

An aerosol-based liquid chromatography/mass spectroscopy interface (MAGIC-LC/MS) has been constructed. This device uses monodisperse aerosol generation, atmospheric pressure desolvation, and aerosol beam separation of solute particles and solvent vapor. The interface may be operated with equal ease on magnetic sector or quadrupole instruments. The device is very simple to operate, and has minimal adjustments for setup. The interface may be connected to the mass spectrometer without modification to the instrument, and allows a complete choice of electron impact or chemical ionization modes. The interface has perfomed well with microbore chromatography, and can be operated with all commonly used normal and reversed phase solvents. Tests with a number of environmentally important compounds, such as carbamate and triazine pesticides and polynuclear aromatic compounds have given detection limits of approximately 100 pg with single ion monitoring, with 1 to 10 ng for full EI scans.

## Hampton University
## Hampton, Virginia 23668

### 355. *Use of Ion Chromatography–D.C. Plasma Atomic Emission Spectroscopy for the Speciation of Trace Metals*

*I.T. Urasa* **$70,000**
*Department of Chemistry* **(18 mo.)**

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. The potential of DCPAES as a chromatographic detector has not been fully developed and exploited. This detection approach has an added advantage in multielement measurement capability suitable for determining metals and nonmetals. In this research the system will be 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 (metals and nonmetals) at a wide range of chromatographic conditions. Work will focus on the study and development of chromatographic conditions and IC-DCPAES coupling mechanisms that allow maximum detection capability.

## University of Houston
## Houston, Texas 77004

### 356. *Mechanisms of Cake Filtration*

*F.M. Tiller, M. Tadros* **$144,300**
*Department of Chemical Engineering*

The theory of particulate separation involving compressible, porous beds or sediments as found in sedimentation, filtration, centrifugation, and expression is studied. The Darcy equation in spatial or material coordinate form must be combined with a differential momentum balance to produce simultaneous equations involving the liquid pressure and the compressive effective pressure. Solution of these equations requires constitutive relations involving permeability, specific flow resistance, and porosity. Different boundary conditions, the presence of gravitational or centrifugal forces, and solid movement in sedimentation lead to different forms of the basic equation. This project aims to unify the theory underlying the different types of solid–liquid separation and to develop techniques for determining empirical parameters involved in the constitutive equation. The structures of beds of dispersed and aggregated uniform, micron-sized particles are related to compressibility. A rough predictive method for calculating parameters in functions relating porosity and permeability to effective pressure has been developed. Quantities used in the correlations include particle size and shape and degree of aggregation. An apparatus for simulating a continuous thickener by partially fluidizing a bed of fine particles has been constructed. Initial cake structure of deposits affected by surface charge, suspension concentration, and agitation is studied in relation to resistance to flow. Pressure distributions are used to study flow mechanisms and fine particle migration. The University of Houston and Martin Marietta Laboratories are cooperating in this research.

## University of Idaho
## Moscow, Idaho 83843

### 357. *The Effect of Electric Fields on Liquid Extraction*

*T.E. Carleson* **$35,000**
*Department of Chemical Engineering*

The objectives of this research are the determination of a theoretical model and the experimental verification of the model of the effect of electric fields on a small-scale liquid extraction column. Various studies with single conducting drops in an insulating medium indicate that an applied electric field can significantly change the drop size and terminal velocity. For an electric field oriented in the direction of gravity and charged drops with a density higher than the continuous phase, the drop size is reduced and velocity increased with an increase in field strength. Incorporation of the electric field force into a force balance on the forming and falling drop results in a fairly good model for prediction of the effect of the electric field on the drop size and velocity. Incorporation of these parameters into a standard mass transfer model of the drop extraction process also appears to allow prediction of the extraction for single drops. A multistage sieve tray extraction column is under construction for determining the effect of an electric field on a drop population and extraction.

## University of Illinois
## Urbana, Illinois 61801

### 358. *Theta Pinch Discharges for Solids Vaporization and Elemental Chemical Analysis*

*A. Scheeline* **$48,800**
*School of Chemical Sciences*

A pulsed, magnetically constricted plasma (theta pinch) is being used for elemental chemical analysis. The pinch is used to heat and compress a plasma, generally of argon. With correct sample placement, the plasma vaporizes a few micrograms of the sample with each pinch. Recently, useful emission has been observed not only from conductive solids (aluminum, stainless steel) and powders (tungsten), but also from a bulk insulator (boron nitride). The sampling of boron nitride (boiling point 3500 K) is the first demonstration that the goals of this research are being achieved. The only other analytical method that can sample bulk insulators without premixing with a conductive powder is laser ablation. Because the sampling is over a larger area with the theta pinch than with laser ablation, reduced sensitivity to problems caused by sample heterogeneity is anticipated. Time gating allows observation of emission by neutral atoms for hundreds of microseconds after ionic emission and continuum emission have disappeared, making low limits of detection likely. Immediate plans are to extend the qualitative successes of the past year to quantitative results.

## Kansas State University
## Manhattan, Kansas 66506

### 359. *Development of a New Novel Hadamard Transform Infrared Spectrometer for Analytical Chemistry*

*W.G. Fateley* **$59,300**
*Department of Chemistry*

We are developing a special Hadamard infrared spectrometer to investigate the heterogeneous nature of substances such as coal samples. A newly designed Hadamard mask is used. A two-dimensional infrared study will investigate the distribution of impurities, structural differences, material properties, and concentration variations in coal and other heterogenous materials. In this study we use a two-dimensional Hadamard fore mask accessory to the HTS spectrometer. The coals serve as the source in an emission experiment and are placed between the focusing optics and the two-dimensional Hadamard fore mask in a transmission experiment. The chemical variations with depth will be investigated in different coal samples. Using the photoacoustic detector and a Czerny-Turner monochromator equipped with an exit Hadamard mask allows depth-profiling of these coal samples. Using subtraction techniques developed in Fourier transform spectroscopy, we will examine the spectra of different depths and the chemical differences between the surface and the bulk of these coal samples. These investigations may be classified as two-dimensional depth spectroscopy. Additional studies involving the development of Fourier transform spectrometer and a Hadamard transform spectroscope for Raman studies are in progress. A Nd:YAG laser is the exciting source. The studies yield important structural information.

## Kent State University
## Kent, Ohio 44242

### *360. Adsorption and Desorption of Hydrocarbons at Low Concentrations*
*R. Madey* **$69,300**
*Department of Physics*

The aim of this research is to study the adsorption and diffusion of gases through porous media adsorber beds. The approach involves calculations based on a mass-balance equation of the quantity of adsorbate adsorbed on an adsorbent, measurements of adsorption isotherms of hydrocarbons on activated carbon and polystyrene beads at selected temperatures, and studies of the dynamics of breakthrough curves with both a step-function and a pulse change of the input concentration. The breakthrough curves of binary mixtures exhibit interference phenomena where the output concentration of the weakly adsorbed component increases above the input concentration until the other component elutes. The project objectives include (1) providing an explanation of interference phenomena and (2) studying adsorption with a first-order irreversible chemical reaction. Since the decay of a radioactive isotope is a first-order reaction, measurements of the transmission of radioactive $^{41}$Ar and stable $^{40}$Ar will permit a study of the effect of dynamic parameters on the steady-state transmission and on the moment of the transmission curve. Transmission is the ratio of the concentration of an adsorbate at the bed outlet to that at the inlet.

## University of Maryland
## College Park, Maryland 20742

### *361. Study of Highly Selective Sorptive Effects with Applications to Paraffins and Petroporphyrin Separations*
*D.H. Freeman* **$60,000**
*Department of Chemistry*

Organic biomarkers are of interest in areas that create a challenge to modern separation science. New sorptive materials and new uses of methodological principles are being studied. These efforts are focused on two goals. The rapidly achieved chemical selectivity of silicalite is being explored. This new sorbent, a zeolitic form of silica, is highly sorptive for the n-alkanes and their monomethylalkane isomers. Dimethylalkanes and other molecules of slightly larger cross sectional diameter are selectively excluded from silicalite. An improved analytical sequence is being developed to examine the methyl group positions in the monomethylalkanes. Such isolations from petroleum source materials may provide a possible indicator of geothermal stress. Similarly, the isolation of petroporphyrins is sought using selectivity multiplying sequences of short HPLC columns (1 to 3 cm length, 200 to 500 plates). Different petroporphyrin groups are isolated. Their tetrapyrrole ring structures are identified by their characteristic Soret band absorption of 400 to 410 nm light. Group subclassification is based on interactions with a series of sorbents being screened for that purpose. A suite of characterized petroleum and shale oil samples will be examined.

## University of Minnesota
## Minneapolis, Minnesota 55455

### *362. Continuous Reaction Chromatography*
*R. Aris, R.W. Carr* **$72,000**
*Department of Chemical Engineering and Materials Science*

Continuous reaction chromatography is a method for carrying out chemical reaction with simultaneous chromatography of reactants and products in a single continuous flow reactor. This can be accomplished by providing relative motion between the chromatographic packed bed and the feedstream. Investigations of the rotating cylindrical annulus for both liquid-phase reaction–solid adsorbent and gas–solid catalytic reactions have been completed. A detailed modeling study of the behavior of a countercurrent moving-bed chromatographic reactor has also been conducted. Experimental tests of a laboratory-scale countercurrent moving-bed reactor are being carried out. Analysis of reaction products is being done by conventional gas chromatography and the performance of the reactor is being compared with theoretical predictions. The simulation of countercurrency by switching the feed between fixed columns is investigated both theoretically and experimentally.

## University of Missouri
## Rolla, Missouri 65401

### *363. An Extraction/Separation Process with Extreme Energy Efficiency*
*S. Friberg, P. Neogi* **$70,000**
*Department of Chemistry*

The purpose of this investigation is to examine the phase equilibria involved in an extraction/separation process with extremely low energy demand. The process uses the temperature-dependent transitions of colloidal association structures in systems of water–polyethylene glycol, dodecyl ethers–aliphatic hydrocarbons to permit spontaneous extraction and separation with a temperature change of only 20°C. The main emphasis is placed on the role of liquid crystals to influence the kinetics of the extraction process.

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

### *364. Competitive Ion Kinetics in Direct Mass Spectrometric Organic Speciation*
*L.W. Sieck* **$137,000**
*Center for Chemical Physics*

This research project involves the measurement of fundamental properties of gas-phase ions, including fragmentation and reaction mechanisms and rates, structures, and the thermochemistry associated with ionization, protonation, and reaction. When appropriate, this information is then used to suggest chemical ionization techniques that incorporate competitive ion kinetics and permit identification and/or assay of specific compounds or classes of compounds occurring in complex organic mixtures. The experimental project uses the National Bureau of Standards pulsed high-pressure mass spectrometer system as the prime facility; an ion cyclotron resonance instrument is also available. Work in progress includes determinations of enthalpies of hydration and solvation of complex anions of the type

$RO^-$ and $RCO_2^-$, as well as systematic studies of the unimolecular kinetics associated with ion pyrolysis.

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

### 365. *Stable Isotope Studies*

*T. Ishida* **$85,000**
*Department of Chemistry*

This project is concerned with fundamental studies of isotope effects and their applications to problems of stable isotope fractionation. The following studies have recently been completed: (1) cell-model analyses of vapor pressure isotope effects in liquid and solid ammonia and in liquid methylene difluoride, and (2) development of a self-contained chemicals recycle system for use in the $^{15}N$ fractionation processes, eliminating the need for external chemical feeds and chemical waste disposal. Current areas of investigation are: (1) basic and developmental studies of heterogeneous catalysts for the hydrogen isotope exchange reaction between water and hydrogen with *in situ* controllable hydrophobicity and *in situ* catalytic activity regeneration; (2) molecular dynamics (MD) simulations of physical spectroscopic properties of liquid and solid ammonia (as a basis for further MD studies of solutions in liquid ammonia) and of catalytic properties of the platinum surfaces for hydrogen isotope exchange reactions; and (3) continued development of zero-point energy additivity tables for organic molecules.

## University of Oklahoma
## Norman, Oklahoma 73019

### 366. *A Study of Micellar-Enhanced Ultrafiltration*

*J.F. Scamehorn,* **$65,800**
*S.D. Christian*
*School of Chemical Engineering and Materials Science*

In micellar-enhanced ultrafiltration, surfactant is added to aqueous streams containing dissolved organics. Aggregates called micelles are formed, into which a very high fraction of the organic solute tends to be distributed. The solution is then passed through an ultrafiltration filter with pores just small enough to prevent the micelles from passing through. The removal of a number of organic compounds has been studied, including phenolics, alcohols, carboxylic acids, aromatic hydrocarbons, and aliphatic cyclic hydrocarbons. In general, the less water soluble the organic, the more effectively it is removed. Solute rejections of >98% have been observed for many compounds of interest in pollution control, with rejections measured as high as 99.8%. The limits of surfactant concentration in the retentate in which the separation operates effectively have been delineated and a gel-point measured. The gel concentration is independent of pressure and membrane pore size. Membrane pore sizes of up to 10 K molecular weight cut-off effectively block micelles.

## Oklahoma State University
## Stillwater, Oklahoma 74078

### 367. *Unsegmented Continuous Flow Sample Processing and Electrochemical Detection and Determination of Gaseous Species*

*H.A. Mottola* **$60,000**
*Department of Chemistry*

This work involves a novel approach to sample processing in determining gaseous pollutants of oxidizing and reducing nature. A continuous-flow unsegmented all-gas carrier system and a segmented liquid–gas interface system will be constructed for sample introduction and transport to the detection/determination port. A regenerable electrode probe based on the redox characteristics of the iron(II) and iron(III) complexes with 1,10-phenanthroline and related ligands will be implemented as the detection device. Several electrodes of the chemically modified type will be constructed and tested. Amperometric and coulometric current measurements will be evaluated for acquisition of the analyte signal for quantitative purposes. Voltammetric studies will provide evaluation of the electrode surfaces generated as part of the work.

## 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* **$135,800**
*Department of Chemistry*

Our recent developments (involving both software and hardware modifications of the Nicolet FTMS-1000 Fourier transform mass spectrometer) now enable us to conduct research in what can be properly termed a complete gas-phase chemical laboratory. Selected ions of interest can be mixed with various reagents and their detailed chemistries monitored through a series of as many as eight reaction sequences. At any point in these sequences, ion structures can be elucidated and fundamental kinetic and thermodynamic parameters of the reactions can be determined. We are currently examining the gas phase chemistry and photochemistry of metal ions, metal ion clusters, and metal ion complexes, all of which have a bearing on the fundamentals of catalysis.

## Rensselaer Polytechnic Institute
## Troy, New York 12181

### 369. *Macrocyclic Ligands for Uranium Complexation*

*K.T. Potts* **$90,000**
*Department of Chemistry*

A computer-aided design (CAD) approach has been used in the design of a series of macrocyclic ligands whose cavity diameters were optimized for the complexation of the uranyl ($UO_2^{2+}$) ion from solutions. These macrocycles, assisted by the "macrocyclic effects" and incorporating "hard" oxygens as the ligating atoms, should also show selectivity for the uranyl ion and give complexes with favorable stability constants. Three principle types of macrocycles have been designed: (1) cycloaliphatic-type systems containing one biureido function and two acyl urea functions; (2) cycloaliphatic-type systems containing three biureido functions; and (3) systems of the above type containing aromatic and heterocyclic subunits. All use oxygen as the ligating atom and have the potential for attachment to polymers such as cross-linked polystyrene. Synthetic sequences leading to these macrocycles involve novel applications of acyl isocyanate chemistry. These applications will provide economical routes to the target macrocycles, which will be studied for their selectivity in absorbing the uranyl ion from homogeneous and heterogeneous systems. The structures of the uranyl complexes, together with their stability constants, will be determined. These macrocycles will all have important potential applications in two main areas of uranium technology: the removal of uranium from waste streams and the development of alternate sources of uranium by extraction from natural waters such as sea water and river systems rich in dissolved uranium.

## San Diego State University
## San Diego, California 92182

### *370. Development and Optimization of Methodologies for Analysis of Complex Hydrocarbon Mixtures*

*R.J. Laub* **$73,100**
*Department of Chemistry*

In this project, the analytical and physicochemical properties of nonelectrolyte solutions are determined and interpreted in terms of solute liquid–gas (GC) and liquid–liquid (LC) activity and partition coefficients as well as gas-phase virial effects. Regressions of the former against the composition of multicomponent solvents are examined from the standpoints of solvent–additive interaction, solvent–solvent self-association, and, (in each case), weak-to-strong solute–solvent complexation. Also of very considerable interest are newly synthesized polymeric side-chain liquid–crystalline (MEPSIL) systems. Those fabricated thus far include several that are nematic over a temperature span in excess of 200°. Others are chiral; while still others appear, simultaneously, to exhibit properties of both types of mesomorphs. The MEPSIL materials also yield unprecedented analytical separations when employed as GC or LC stationary phases.

## Syracuse University
## Syracuse, New York 13244

### *371. Mechanisms of Gas Permeation Through Polymer Membranes*

*S.A. Stern* **$80,000**
*Department of Chemical Engineering and Material Sciences*

The project objective is to investigate the significant changes that commonly occur in the mechanisms of gas transport in and through polymer membranes at their glass-transition temperature (Tg). To explore the character of these changes, permeability, diffusion, and solubility coefficients for $CH_4$, $C_2H_6$, *n*ta/-$C_4H_{10}$, and $CO_2$ in poly(*n*-butyl methacrylate)(P*n*BMA) are being determined at pressures up to 25 atm and in the temperature range from -10 to 50°C, which encompasses the Tg of the polymer (27 to 35°C). Contrary to expectations, no changes in the pressure and temperature dependence of the permeability, diffusion, and solubility coefficients were observed as the temperature was lowered below Tg. Moreover, the gas–polymer systems studied did not exhibit below Tg the usual dual-mode sorption behavior of gases in glassy polymers. The present results are probably the first well-documented exceptions to dual-mode sorption behavior, and may be due to the small difference in the coefficients of thermal expansion of P*n*BMA above and below its Tg. A previously reported change in the mechanisms of transport of some gases in P*n*BMA at its Tg was an artifact caused by slow relaxation phenomena in the polymer. It is possible that the gas–P*n*BMA systems studied will exhibit dual-mode sorption behavior at much lower temperatures.

### *372. Reactor Analysis for Selective Metal Ion Extraction in Liquid Dispersions*

*L.L. Tavlarides* **$120,000**
*Department of Chemical Engineering and Materials Science* **(18 mo.)**

The goal of this project is to provide fundamental models for the rational design of liquid extraction processes to predict conversion and selectivity in the hydrometallurgical extraction of metals. The dispersed phase model we developed incorporates the details of the thermodynamic chemical equilibria, chemical kinetics, mass transfer processes, and the effects of droplet mixing. Thermodynamic two-phase equilibrium data and kinetic data have been obtained and analyzed to develop models to predict interfacial flux in the presence of mass transfer for the $Co^{+2}$–$NO_3^-$/-di(2-ethylhexyl) phosphoric acid toluene system. A specially designed Lewis cell contactor was used for the latter. A two-film theory model with an appropriate reaction mechanism corroborates experimental data indicating that the reaction occurs in the aqueous film. The efficacy of the dispersed phase model to predict conversion and selectivity for continuous flow stirred tank extractors (CFSTE) will be determined. Bivariate drop size/concentration data for this hydrometallurgical system will be obtained in a fully instrumented CFSTE. A specially designed capillary laser spectrophotometer has been constructed and will soon be commissioned for this purpose. The mass transfer/reaction model will be used in the dispersed phase model to analyze experimental results from the CFSTE to ascertain the impact of operation conditions (and dispersed phase mixing) on conversion, and prove the utility of such models to predict CFSTE performance. The dispersed phase models will be extended to analyze mutistage extractor performance for various configurations. This general analysis will be made for the $Co^{+2}$–$Ni^{+2}$ multiple metal system; however, it will have applicability to other complex hydrometallurgical systems.

### *373. Particle Deposition in Granular Media*

*C. Tien* **$182,500**
*Department of Chemical Engineering and Materials Science* **(24 mo.)**

The principal objective of this study is to elucidate the various phenomena arising from the flow of aerosol suspensions through and the deposition of aerosols in granular media. The project focuses on (1) experimental investigation of the transient behavior of aerosol filtration in granular filters, (2) development of algorithms for predicting aerosol filtration in fluidized beds, (3) aerosol collection in magnetically stabilized fluidized filters, (4) *in situ* observation of aerosol deposition in two-dimensional model filters, and (5) experimental study of cross-flow moving-bed granular filtration.

## University of Tennessee
## Knoxville, Tennessee 37996

### *374. Systematic and Structural Studies of Polymeric Extractants for the Separation and Recovery of Metal Ions*

*S.D. Alexandratos* **$72,500**
*Department of Chemistry*

A new class of resins, dual-mechanism bifunctional polymers, has been synthesized. The primary application for these resins is recovery of metal ions from aqueous streams using solid–liquid extraction schemes. They can be effectively used in hydrometallurgical processes and are especially important for strategic metal recovery. These resins consist of a polystyrene support network on which are bonded two different phosphorus groups. When brought in contact with a metal-containing aqueous stream, they ion-exchange with the metal cation and then reduce it, allowing the isolation of zerovalent metal. These high-capacity, stable resins may be produced in two steps from polystyrene beads and show a great affinity for transition metal ions; they will absorb 70% of the mercuric ions in solution under conditions where commercial sulfonic acid resins absorb 25% and carboxylic acid resins absorb 15%. Additionally, these resins release the mercury after the reduction reaction, allowing it to collect in a reservoir apart from the resin itself. The selective recovery of metallic silver and gold from aqueous solutions has also been accomplished. Current research involves the synthesis of (1) new resins for the recovery of lanthanides and actinides and (2) the production of new high-stability membrances for metal-ion recovery processes.

### *375. Capillary Separations with Calorimetric Absorbance Detection*

*M.J. Sepaniak* **$62,000**
*Department of Chemistry*

The main focus of this research is capillary LC as a practical separation technique for volume-limited complex samples and for difficult to resolve compounds. Detectors (primarily thermo-optical) that satisfy the ultralow volume and high sensitivity requirements of capillary LC are a crucial aspect of this research. Narrow-bore (i.d.s. of about 20 $\mu$m) open capillary columns have been prepared using bonded stationary phases and stationary phases dynamically formed through the inclusion of a cationic surfactant in the mobile phase. The dynamic open capillary columns have exhibited efficiencies as high as 100,000 plates for 5 m columns. Electrokinetic capillary separations, using micellar "pseudostationary" phases, have also been performed. Column efficiency and selectivity are investigated. Single beam thermal lens detection has been used with open capillary LC. Minimum detectable absorbances of about $3 \times 10^{-5}$ were obtained. Access to the ultraviolet spectral region is accomplished via double beam photothermal refraction detection, using a tunable pulsed laser as the heating source. Although reproducibility has not been satisfactory, minimum detectable absorbances of less than $10^{-5}$ have been achieved for detection with slurry-packed, fused-silica capillary columns. Sheath flow cells are currently used in conjunction with multidimensional, laser-based detection, to improve the pulsed laser mode of thermo-optical detection and to provide alternate selective detection schemes (e.g., fluorescence and multiphoton photoionization).

## 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* **$80,000**
*Department of Chemical Engineering*

This project involves a concerted experimental program to develop advanced polymeric membranes for gas separation applications. Focus is on the interpretation of high-pressure pure and multicomponent gas sorption and transport data to be collected for a series of novel polymers to be synthesized as part of the project. The research builds on earlier work showing remarkably high permeabilities and selectivities for important gas pairs using rigid, high glass transition polymers that contain bulky groups and other features to prevent tight segmental packing. The study will include the pressure regime in which serious plasticization (softening) is anticipated, and mixed gas permeability measurements will track the loss in selectivity as the various polymers become plasticized. Existing theories and types of correlations for the fundamental sorption and diffusion coefficients of the various penetrants will be tested for these novel rigid molecularly open materials. Such tests will indicate the suitability of these theories and correlations to guide material selection and design of advanced gas separation modules.

## Texas A and M University
## College Station, Texas 77843

### *377. Laser-Ion Beam Photodissociation Techniques*

*D.H. Russell* **$97,500**
*Department of Chemistry* **(15 mo.)**

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 being developed by using model chemical systems such as $C_6H_6^+$ and $C_4H_4^+$, which are relatively well characterized, and new systems such as $Fe_x(CO)_y^+$ and similar ionic cluster fragments. 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 $B_{12}$, small peptides, and glycopeptides (1500 to 4000). These studies are performed on modified analytical instruments (e.g., Kratos MS-50TA and MS-902) as well as a Fourier transform mass spectrometer (Nicolet FTMS-1000).

## University of Texas at El Paso
## El Paso, Texas 79968

### *378. Macrocyclic Lanthanide Ion Selective Reagents*

*C.A. Chang* **$51,900**
*Department of Chemistry*

Solvent extraction behavior of lanthanum(III) and neodymium(III) has been investigated using thenoyltrifluoroacetone (TTA) as extractant in the presence of 1,7-diaza-4,10,13-trioxacyclopentadecane-N,N′-diacetic acid

(DAPDA) and 1,10-diaza-4,7,13,16- tetraoxacyclo octa decane-N,N′-diacetic acid (DACDA) as macrocyclic ionophores. DAPDA and DACDA were chosen in view of their unique complexation towards lanthanides. $Ln(TTA)_3$ is the dominating species extracted at pH $\leq$ 5.0 and Ln(DAPDA/DACDA)TTA is possibly the dominating species at pH $\sim$ 7.5. The extraction of ternary complexes of La(III) is greater in the case of DAPDA and smaller in the case of DACDA as compared to the extraction of corresponding ternary complex of Nd(III). This indicates that charge density, size of the metal ion, cavity size, and stereochemical constraint of the ligands are important in determining the selectivity of solvent extractions. An Eu(III) laser luminescence excitation spectroscopic technique has been used to study the solution structures of Eu-DAPDA/DACDA complexes. For the Eu(III)–DAPDA complex, only a single species is present in aqueous solution for which two inner-spere coordinated water molecules are present. For the Eu(III)–DACDA complex, two 1:1 species are present that appear to be in rapid equilibrium with each other with at least one inner-sphere coordinated water molecule. These data are consistent with the thermodynamic, kinetic, and solvent extraction studies. Currently, we are extending our understanding of these systems by using NMR and single crystal x-ray diffraction techniques for solution and solid-state structures.

## Texas Tech University
## Lubbock, Texas 79409

### *379. Use of Functionalized Surfactants in Flame Atomic and Luminescence Analysis*

*D.W. Armstrong* **$65,000**
*Department of Chemistry and Biochemistry*

A new technique of micelle-mediated resonance Raman spectroscopy (MMRRS) has been developed in our laboratory. Ordinary Raman scattering spectrometry produces vibrational spectra that provide abundant information on the structure of molecules. The major shortcoming of this potentially powerful technique is the inherent weakness of the Raman signal. Laser excitation on an electronic absorption band can enhance the weak Raman signal (i.e., a resonance effect). Unfortunately, this frequently produces highly fluorescent backgrounds that negate the resonance Raman signal. Using specially functionalized micelles we have made resonance Raman spectroscopy into a sensitive and generally applicable technique in which an analyte's luminescence properties are no longer of major concern. There are five modes of micellar action, all of which can produce beneficial effects. There is frequently a synergistic effect when two or more modes of action occur at one time. We are currently evaluating the mechanistic aspects of this work and developing several practical applications.

### *380. Metal Ion Complexation by Ionizable Crown Ethers*

*R.A. Bartsch* **$82,000**
*Department of Chemistry and Biochemistry*

The goals of this research are the synthesis of lipophilic crown ethers with pendant ionizable groups and the application of these compounds for selective metal ion complexation. A variety of lipophilic ionizable crown ethers are being prepared in which the following structural features are systematically varied: (1) the size of the polyether cavity; (2) the number and types of ethereal oxygens in the crown ether ring; (3) the attachment site(s) for lipophilic groups; (4) the presence or absence of aromatic groups as polyether ring substituents; and (5) the type of ionizable group. The ionizable functions include carboxylic, phosphonic, and sulfonic acid groups. The efficiencies and selectivites of these lipophilic ionizable crown ethers in competitive solvent extraction, liquid surfactant (emulsion) extraction, and bulk liquid membrane, and polymer-supported liquid membrane transport of alkali metal, alkaline earth, and transition metal cations are being assessed.

### *381. Novel Approaches to Ionic Chromatography*

*P.K. Dasgupta* **$87,500**
*Department of Chemistry and Biochemistry* **(15 mo.)**

The project objective is to develop analytical methodology for high-resolution, high-sensitivity chromatographic analysis of ions. In pursuing membrane-based chromatographic applications, we have developed dual membrane devices that can exchange several hundred microequivalents of alkali metal ions per minute and display negligible chromatographic dispersion. We have fabricated ultrathin asymmetric supported tubular membranes using commercially available porous polymer tubular membranes as the support matrix and depositing a thin layer of silicone rubber or polymeric ion exchanger material thereon. In conjuction with polymeric regenerants, these membranes open a heretofore unexplored vista of performance. To facilitate the development of chromatographic analysis of metal ions with optical detection, we have developed a unique gradient FIA multidimensional detection system that permits the evaluation of metal–ligand and proton–ligand equilibrium constants by a single injection into a flowing stream. Extensive studies have been conducted on the fluorescence properties of metal chelates of 8-hydroxyquinoline-5-sulfonic acid (sulfoxine) based on these studies. Chromatographic methods using sulfoxine in the eluent or in conjunction with newly developed membrane-based postcolumn reaction systems have been developed. Subpicomole detection limits are attainable for a number of metal ions.

## University of Utah
## Salt Lake City, Utah 84112

### *382. Fourier Transform Photoacoustic Spectroscopy*

*E.M. Eyring* **$78,000**
*Department of Chemistry*

Microphonic photoacoustic spectroscopy (PAS) has proven to be a useful analytical tool for qualitative identification, and in favorable situations, quantification of chemical species adsorbed at a gas–solid interface or at shallow depths (< 1 mm) in the bulk solid. Among the disadvantages of the technique are its unsuitability for detection of fast transient chemical species or work at high gas pressures and under vacuum and the difficulty of microphonic measurements at elevated temperatures. Two other photothermal spectroscopies, photothermal beam deflection (PBD) and photothermal radiometry (PTR), have lately emerged that appear capable of circumventing these limitations. FT-IR/PBD spectral studies of organic polymers selected for their opacity and comparative chemical simplicity are being carried out over an extended range of temperatures and pressures. The objective is the determination of the basic chemistry required for FT-IR/PBD spectroscopy to surpass

FT-IR/PAS in usefulness. A by-product of the resulting infrared spectral information will be an improved understanding of doping of semiconducting organic polymers. Semiconductor to metal-phase transitions in solids are being reexamined by PTR using pulses of visible radiation from an argon-ion laser to *excite the sample and HgCdTe detectors to measure emitted* radiation.

### 383. *Hydrophobic Character of Nonsulfide Mineral Surfaces as Influenced by Double Bond Reactions of Adsorbed Unsaturated Collector Species*

*J.D. Miller* **$72,000**
*Department of Metallurgy and Metallurgical Engineering*

The separation of nonsulfide minerals from ore is frequently accomplished by froth flotation using unsaturated fatty acids as collector. Variables such as temperature, oxygen partial pressure, and solution chemistry may have a significant effect on flotation rate and the hydrophobic character of certain nonsulfide minerals. Bubble attachment measurements at a fluorite ($CaF_2$) surface have shown that attachment times decrease by an order of magnitude at higher temperature and higher oxygen partial pressure when compared to ambient conditions. Adsorption density measurements indicate that chemisorption reactions occur between oleate and the fluorite surface. At higher temperature and oxygen potential the adsorption density increases slightly. More important, however, is the finding from infrared spectroscopy that the carbon–carbon double bond is reduced in intensity under these conditions, indicating a specific interaction of the adsorbed unsaturated collector species. Study of the nature of this interaction is in progress; it has been established that the oleate interaction at the fluorite surface consumes oxygen. It is thought that the interaction may involve surface polymerization; if such a reaction is operative, 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.

## University of Virginia
## Charlottesville, Virginia 22901

### 384. *Glow Discharge as an Atomization and Ionization Source*

*W.W. Harrison* **$157,200**
*Department of Chemistry* **(24 mo.)**

This project studies the glow discharge as an atomization and ionization source. Focus is on development of the discharge as a source for the trace element analysis of solids by mass spectrometry and atomic emission. The hollow cathode plume has been demonstrated as an effective source for bulk solid conductors and also nonconductors mixed with a conducting matrix such as powdered copper, silver, or graphite. We can obtain qualitative and quantitative analysis to the sub-ppm level. The effects in compacted samples of varying the matrix/sample ratio show that 3/1 is quite satisfactory. Few molecular interferences are seen. Samples prepared in this manner may be analyzed by HCP emission or HCP mass spectrometry. By comparing spectra obtained from each under varying conditions of current and pressure, we are gaining a better understanding of excitation and ionization mechanisms. A tunable dye laser is also used with our glow discharge sources to probe relevant atomic states. Depopulation of neon metastable states shows a strongly negative ion response, implicating the $Ne^*$ in the ionization step. We are also studying the effect of ion exit orifice size on beam formation and signal sensitivity. Several configurations of skimmer cones are also being explored for maximum ion throughput.

## University of Wyoming
## Laramie, Wyoming 82071

### 385. *Solid Surface Luminescence Analysis*

*R.J. Hurtubise* **$84,000**
*Department of Chemistry*

The main goal of this project is to develop a basic understanding of the physical and chemical interactions that enhance room-temperature fluorescence and room-temperature phosphorescence from organic compounds adsorbed on solid surfaces. Several spectral techniques are used to clarify the interactions. In addition, the effects of moisture, gases, and temperature on the fluorescence and phosphorescence quantum yields and the phosphorescence lifetimes of adsorbed compounds are investigated. A variety of luminescence parameters are calculated, such as triplet formation efficiencies and the rate constants for phosphorescence. Results will help to determine whether the luminescent molecules are held rigidly or if the solid matrix prevents collisions with oxygen, water, or impurity molecules. Other work involves the use of cyclodextrins to induce room-temperature luminescence from adsorbed compounds and the use of solid-surface luminescence to study the interactions of solvents with silica gel.

# Chemical Engineering Sciences

## American University
## Washington, District of Columbia 20016

### 386. *Theory of Condensable Gases*

*J.A. White* **$90,000**
*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, unreliable, or insufficiently accurate.

## Brigham Young University
## Provo, Utah 84602

### 387. *Thermodynamic Study of $CO_2$–Organic Compound Interaction at High Pressures and Temperatures*

*J.J. Christensen, R.M. Izatt* **$100,000**
*Department of Chemical Engineering* **(15 mo.)**

The primary objective of this project is to elucidate the energetics associated with the interaction of $CO_2$ and freons with selected organic compounds under temperature-pressure conditions where either one or more of the components is in its supercritical region. The quantities measured are heats of mixing ($H^E$) of binary mixtures using flow calorimeters. The temperature and pressure ranges covered are 285 to 673 K and 8 to 12.5 MPa, respectively. The data allow evaluation to be made of the effect of temperature and pressure on the magnitude of $H^E$ and on phase splitting. The occurrence of phase splitting is detected by discontinuities in the $H^E$ curves, and the phase compositions are calculated from the mole fraction values at the points of discontinuity. In the critical region, large variations in $H^E$ are found with temperature, pressure, and component mole fraction. Moreover, the $H^E$ values show large positive or negative values as the critical region is spanned. The large changes in $H^E$ have been modeled successfully using the Andrews-Soave and other equations of state. The eventual goal is to elucidate the chemistry occurring in supercritical fluid processes.

## University of California
## Davis, California 95616

### 388. *Statistical Modeling and Analysis of Chemically Reacting Turbulent Flows*

*H.A. Dwyer, W. Kollmann* **$85,000**
*Department of Mechanical Engineering*

The project objective is to develop new turbulent closure models for variable density turbulent flow and turbulent diffusion flames. The methods used to accomplish these goals are (1) physical and mathematical modeling and (2) sensitivity analysis. The modeling techniques are built around the density-velocity statistical correlations and the use of Monte Carlo simulations of scalar transport. Previous research has centered on the turbulent diffusion jet, but a new effort on the turbulent boundary layer diffusion flame has been initiated. The boundary layer studies are showing a much different turbulent flow structure, and this structure will offer a more difficult and complete test of previous closure assumption. The sensitivity analysis has been completed for the jet diffusion flame, and has exhibited clearly the relationships between turbulent flow structure and statistical closure assumptions.

## University of California
## Santa Barbara, California 93106

### 389. *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 under conditions of forced concentration oscillations. Compared to 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 is expected to provide 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. At moderately high pressures ($\sim$4MPa) and at typical operating temperatures (650 to 750 K) in a plug-flow configuration, ammonia production rate is diminished (compared to optimal steady state) when the cycling operation is between pure hydrogen and nitrogen. This is because the catalyst deactivates reversibly in the presence of the pure species. When cycling between $N_2$–/$H_2$ mixtures with appropriate cycle times, cycle splits, and composition amplitudes, significant enhancements of ammonia production rate occur. Nitrogen storage in the bulk-phase of the iron catalyst has an important influence on the surface kinetics. For methanol synthesis from CO and $H_2$, a steady-state kinetic model has been developed and contains only five parameters (two of which are independently determined). The model includes the methanol contribution from $CO_2$, which stabilizes the catalyst against $CH_4$ production.

## University of California/San Diego
## La Jolla, California 92093

### 390. *Premixed Turbulent Combustion*

*P.A. Libby* **$78,300**
*Department of Applied Mechanics and Engineering Sciences*

This project involves two areas of active investigation. One concerns the structure and properties of laminar premixed flames subject to general three-dimensional strain fields that arise in turbulent flows. This work is conducted in collaboration with Princeton University. Current study is on the special saddle point case for which a new limiting treatment, not previously considered even for boundary layer flows, is under investigation. Final numerical work is under way. A second study concerns the extension of the Bray-Moss-Libby model of premixed turbulent combustion to incorporate space and time information. The goal of this research is development of a new model for the mean rate of creation of product in premixed turbulent combustion. Present models are highly intuitive and difficult to rationalize. An equation is being developed for a single-point two-time correlation of a two-valued function that defines the state of the gas in a premixed flow. This work is conducted in collaboration with Cambridge University and with ESMA, Poitiers, France.

## Clarkson University
## Potsdam, New York 13676

### 391. *Analysis and Computer Tools for Separation Processes Involving Nonideal Mixtures*

*A. Lucia* **$84,000**
*Division of Research*

Computer tools are generally required for process and control systems design tasks because of the inherent nonlinearity of the equations that model separation processes involving nonideal homogeneous or heterogeneous multicomponent mixtures. Process analysis can often play an important role in the development of reliable computer tools for design, and in the design task itself. Very little research has focused on the analysis of separation processes involving homogeneous mixtures. One objective of our work is to study the question of the uniqueness of existing computer tools and/or the development of new algorithms for the reliable solution of these problems. For separation processes involving heterogeneous mixtures, far fewer computer tools exist to support the design and simulation tasks. The goal here is to develop reliable and efficient computer tools for these separation processes based on insights provided by the structure of ternary phase diagrams for these systems. We also propose (1) to develop an analysis to aid in developing these tools and (2) to address certain computational and theoretical aspects such as the multiplicity of false solutions, efficient and reliable equation solution, and local uniqueness.

## Columbia University
## New York, New York 10027

### 392. *Interaction of Turbulence and Chemical Reactions*

*R. Chevray* **$92,800**
*Department of Mechanical Engineering*

Flow in a two-dimensional mixing layer is utilized to study a well-known reaction with simple kinetic scheme. The flow represents a well-defined turbulent situation, and additional complexities of finite heat release are avoided by use of small concentrations for the reaction chosen ($NO + O_3 \rightarrow NO_2^* + O_2 \rightarrow NO_2 + h\nu + O_2$). Large Reynolds numbers, small dilution numbers, large reaction speed numbers, and several concentration rations are investigated. Conditional and conventional measurements are made of mean and fluctuating quantities for both the velocity and concentration fields by laser Doppler anemometry and fiber optics absorption spectroscopy, respectively. Simultaneous cinefilm recording has been conducted to determine the convection velocity of the interface and hence the entrainment. Numerical simulation is set up to model directly the equations describing the evolution of the species concentration in the shear layer.

## Cornell University
## Ithaca, New York 14853

### 393. *Experimental and Theoretical Studies of Dense Fluid Mixtures*

*W.B. Streett, K.E. Gubbins* **$122,000**
*School of Chemical Engineering* **(18 mo.)**

The primary goals of this research are: (1) to carry out wide-ranging thermophysical property measurements for 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 measurements of the PVT properties of $CF_4$, $CHF_3$, and $CCl_4$ at pressures to 1000 bars. The studies of $CCl_4$ made during the past year are the first to use the redesigned and reconstructed direct-weighing PVT apparatus and the new velocity of sound apparatus for dense fluids. The direct-weighing apparatus is designed to work from room temperature to 600°C and from 0 to 2000 bars, and the velocity of sound apparatus is designed for work from -150 to 250°C and from 0 to 4000 bars. Measurements are in progress on normal- and neopentane. Theoretical work has included applying various equations of state to the PVT data on $CF_4$ and $CHF_3$ to test the applicability of different kinds of equations of state to fluid data covering a wide range of conditions. A new form of the Tait equation of state for liquids has been developed to give an accurate description of the data for $CCl_4$.

## University of Delaware
## Newark, Delaware 19716

### 394. *The Generalized van der Waals Theory of Pure Fluids and Mixtures*

*S.I. Sandler* **$65,000**
*Department of Chemical Engineering* **(15 mo.)**

The generalized van der Waals theory provides an excellent framework for understanding the basis for applied thermodynamic models currently in use and deriving new, improved models with potential application to heavy oils, coal liquids, and other synthetic fuels. Using a form of the generalized van der Waals partition function that we developed, we now understand the molecular-level assumptions explicit or implied in current thermodynamic models. Further, using computer simulation and integral equation theory, we can test these assumptions, establishing the theoretical validity of some and errors in others, especially some of the recently proposed local composition models. We can also make significant improvements in several models using the combination of the generalized van der Waals theory, integral equation theory, and computer simulation. Work focuses on developing new equations of state, mixing rules, and activity coefficient models for mixtures of molecules of widely differing size and functionality. An important feature of these models will be their firm theoretical basis and broad range of validity.

## University of Florida
## Gainesville, Florida 32611

### 395. *Theoretical and Experimental Investigations of Fluctuation Thermodynamic Properties of Liquid Solutions*

*J.P. O'Connell* **$166,000**
*Department of Chemical Engineering* **(24 mo.)**

Fluctuation solution theory will be developed for analysis and application to strongly nonideal liquid mixtures, including electrolytes. The work includes theoretical analysis, correlation, and experimental measurement using ultracentrifuge equilibrium distribution and liquid volumes over wide ranges of conditions. The results will provide benchmarks for both complete equations of state and statistical mechanical and computer simulation treatments of such systems. In addition, useful correlations will be completed for process design in important energy-related processes such as fossil fuel recovery, high-pressure reaction and separation systems (including coal conversion and petrochemical hydrogenation), energy storage devices, extraction and crystallization devices (as in hydrometallurgy), industrial waste processing, and geologic systems for geothermal power production and mining. The project objectives are (1) to complete a theoretical basis for properties of liquids that is rigorous while leading to useful correlations and (2) to establish both a formulation and a data base that others can use for sensitive comparisons with their methods for strongly nonideal liquids. Present results include a correlation for pressure effects on liquid volume over wide ranges of conditions and for every type of substance, a correlation for partial molar volumes at infinite dilution of salts in water to high pressures and temperatures, initial ultracentrifuge sedimentation data, and an analysis showing that light scattering is a poor technique for obtaining thermodynamic properties of liquids.

## University of Illinois
## Chicago, Illinois 60680

### 396. *Development of the Analytic Variational Inequality Minimization (VIM) Equation of State*

*G.A. Mansoori* **$99,000**
*Department of Chemical Engineering* **(18 mo.)**

This research concerns the development of an analytic equation of state for polar, quantum and associated fluids, and fluid mixtures of practical interest. The approach is based on the variational inequality minimization (VIM) theory of statistical mechanics. The objectives of this research include the following: (1) extension of the VIM equation of state to pure fluids of polar and associated molecules due to hydrogen bonding; (2) extension of the applicability of the VIM equation of state to quantum fluids; (3) calculation of a set of intermolecular potential energy parameters based on the VIM theory for use in the VIM equation of state; and (4) extension of the VIM equation of state to mixtures.

## Johns Hopkins University
## Baltimore, Maryland 21218

### 397. *Prediction of Thermodynamic Properties of Coal Derivatives*

*M.D. Donohue* **$80,000**
*Department of Chemical Engineering*

The purpose of this project is to develop an equation of state to predict the thermodynamic properties of coal derivatives. The equation is based on perturbed hard-chain theory, but includes additional terms for multipole interactions. The equation allows prediction of vapor pressures, densities, and solubilities for a wide range of organic molecules including multiringed aromatics. Pure component and mixture parameters are determined from experimental data when available; a group-contribution correlation is being developed to allow prediction of parameters for systems where no experimental data are available. The applicability of the new equation to supercritical fluid extraction is being studied. Hydrogen-bonding effects are taken into account to predict properties of systems containing $H_2O$, alcohol, and so forth. High-pressure vapor–liquid equilibrium measurements for $CO_2$–aromatic binary mixtures are made.

## Louisiana State University
## Baton Rouge, Louisiana 70803

### 398. *Molecular Dynamics Studies of Aromatic Hydrocarbon Liquids*

*E. McLaughlin* **$74,400**
*Department of Chemical Engineering* **(18 mo.)**

This research is concerned with the molecular dynamics investigation of aromatic hydrocarbon liquids and their mixtures. Focus is on the simulation of aromatic mixtures encountered in dense coal-derived chemicals, such as naphthalene and phenanthrene, in aromatic solvents such as benzene and toluene. Previous computer simulations have been limited to atomic and molecular fluids and their mixtures. The objective is to develop predictive models for determining the properties of complex aromatic liquids encountered in heavy crudes and/or coal processing.

## Massachusetts Institute of Technology
## Cambridge, Massachusetts 02139

### 399. *Thermodynamics and Rate of Methanol Conversion to Hydrocarbon on Zeolites*

*R.A. Alberty* **$168,400**
*Department of Chemistry* **(24 mo.)**

The objective of this project is to determine the extent to which thermodynamics can account for the distribution of products in the gasoline produced from methanol using zeolite catalysts, and the way in which deviations from equilibrium can be accounted for in terms of rate constants. These calculations are made using isomer groups and linear restrictions in a general equilibrium program. Calculations are made for various temperatures, pressures, catalyst selectivity, and extent of reaction. In order to make these calculations, tables of isomer group thermodynamic properties are produced, and the Benson method is used to augment literature data. Thermodynamic data on higher isomer groups are obtained by linear extrapolation. New methods for making chemical equilibrium calculations using homologous series groups and continuous thermodynamics are being developed. The Gibbs energy of formation of all the isomer groups in a homologous series may be calculated for a fixed ethylene partial pressure. This makes it possible to express the equilibrium distribution as an analytic function of the carbon number. Thus the carbon number contributing the largest weight fraction for given conditions can be obtained without calculating the whole distribution using a general equilibrium program.

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

### *400. Experimental and Theoretical Study of the Thermophysical Properties of Fluid Mixtures*

| | |
|---|---|
| *W.M. Haynes* | **$234,000** |
| *Thermophysics Divison* | |

The primary goals of this project are to increase basic understanding of the behavior and properties of complex fluid mixtures, and to develop theoretically based and widely applicable predictive techniques. These objectives are attained by combining experimental measurements with theory and correlation. PVT data, and subsequent correlations, have been obtained for $H_2S$, methanol, and benzene at temperatures to 725 K and pressures to 35 MPa; toluene meaurements are in progress. Dew-bubble point measurements have been performed on methanol–water mixtures at temperatures to 600 K; VLE data have been obtained for binary mixtures of $CO_2$, $nC_4H_{10}$, $iC_4H_{10}$, and R13 at temperatures to 400 K. Viscosity and heat of mixing experimental and modeling studies are used to quantify the problem of association in undefined mixtures, such as coal liquids. All of these measurements are selected on the basis of their usefulness in developing predictive models. Recent theoretical efforts emphasize two areas: (1) development of predictive models for thermophysical properties of complex fluid mixtures using equilibrium and nonequilibrium molecular dynamics and (2) rheological studies of non-Newtonian behavior of a supercooled liquid under shear is studied using computer simulation and neutron scattering. This should give information on the relationship between the simple and complex fluid and on the nature, and possibly a definition, of complexity in fluid behavior.

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

### *401. Transport and Phase Equilibria in Multicomponent Fluids*

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|---|---|
| *J.M. Kincaid* | **$90,000** |
| *Division of Thermophysics* | |

The purpose of this project is to develop and implement simple, accurate techniques to treat the transport and phase transition properties of multicomponent systems. The main focus has been: (1) to develop a thorough characterization of the Enskog theory of hard-sphere mixtures and to determine how the hard-sphere theory can be used to predict the transport coefficients of real fluids and (2) to develop new methods for solving the phase equilibrium conditions of multicomponent systems based on the so-called polydisperse (continuous) fluid formalism. Recent progress includes: (1) a complete analytical exposition of the Enskog theory for mixtures; (2) a thorough study of the thermal and mutual diffusion coefficients of binary and ternary mixtures; (3) a mathematical study of polydisperse fluids demonstrating the ways in which the polydisperse formalism is equivalent to the usual multicomponent fluid approach; (4) the solution of two common phase equilibrium problems: solvent + polydisperse impurity and the nearly monodisperse fluid; and (5) a derivation of the critical-point conditions for a polydisperse fluid.

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

### *402. Thermophysical Properties of Multiphase Systems*

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|---|---|
| *G.R. Stell* | **$180,000** |
| *Department of Mechanical Engineering* | **(24 mo.)** |

Ongoing research to obtain the transport properties of fluids and fluid mixtures in analytically tractable form has continued. Two general approaches have been used. The first is a conditional-probability approach that yields a description of solvent–solute collision involving reduced mass and collision diameter renormalized by the presence of the solvent background. In the limit of identical solute and solvent particles, this results in a new pure-fluid theory as well. A second general approach is information theoretic, based on the maximization of entropy subject to increasingly refined constraints. This yields a sequence of successively more refined versions of a kinetic variational theory. When the pair potential includes a hard-sphere reference-potential term, the theory can be further improved by insertion of an improved treatment of the correlation induced by core–core collisions, yielding a sequence of kinetic reference theories. General expressions for transport coefficients from the variational and reference theories have been obtained and are being quantitatively evaluated. A study of the thermophysical properties of fluids near a critical point has also been initiated.

## Ohio State University
## Columbus, Ohio 43210

### *403. Molecular Orbital Studies of the Bonding in Heavy-Element Organometallics*

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|---|---|
| *B.E. Bursten* | **$44,600** |
| *Department of Chemistry* | |

Our previous research has established the X$\alpha$–SW molecular orbital method with quasi-relativistic corrections as a viable electronic structure tool for the study of organoactinide systems. We have initiated molecular orbital investigations into several aspects of organoactinide chemistry. The comparative bonding capability of small molecule substrates such as carbon monoxide, phosphines, or isonitriles is under way through an investigation of the U(III) systems $(\eta^5\text{-}C_5H_5)_3UL$. These studies are closely related to our previous ones on U(IV) and Th(IV) organometallics, and will also relate to calculations on model systems that contain uranium-to-carbon and uranium-to-nitrogen multiple bonds. Recent reports of molecules containing direct metal–metal bonds between an actinide metal and a transition metal have led to several questions concerning the comparative roles of the actinide 5f and 6d orbitals in the metal–metal bonding. We are investigating these through calculations on molecules containing unsupported metal–metal bonds, such as $(\eta^5\text{-}C_5H_5)_2Th(X)\text{–}Ru(\eta^5\text{-}C_5H_5)(CO)_2$. We are using our calculations to investigate the electronic structural constraints on the synthesis of molecules that contain direct multiple bonds between two actinide centers. Calculations on hypothetical molecules such as $U_2(CH_3)_6$ are indicating possible routes to the design of ligand systems that will be capable of supporting direct uranium–uranium bonds.

## University of Pennsylvania
## Philadelphia, Pennsylvania 19104

### *404. Thermodynamics of Systems of Very Many Components*

*E.D. Glandt* **$174,500**
*Department of Chemical Engineering* **(24 mo.)**

This theoretical and computational project deals with thermodynamic and structural behavior of polydisperse fluid mixtures such as liquid fuels and polymer solutions and melts. The continuous Lennard-Jones model substance is an appropriate first representation of the former. A perturbation theory was developed for narrow cuts, while Monte Carlo computer simulations are the approach chosen to test the theory and to describe the properties of very wide distributions like those encountered in reservoir modeling and in crude liquids in general. A very important aspect of phase equilibrium involving wide distributions is the prediction of the dew point, as it is affected by the presence of a tail of heavy components. Accordingly, the focus of these simulations is the calculation of distributions of the activity coefficients. A generalization of Widom's average potential theory was developed that is specific to the polydisperse case, and is being compared with existing techniques.

## Purdue University Research Foundation
## West Lafayette, Indiana 47907

### *405. Gas–Liquid–Liquid Equilibria in Mixtures of Water, Light Gases, and Hydrocarbons*

*K.C. Chao, H.M. Lin* **$70,000**
*School of Chemical Engineering*

The objective of this research is to investigate the phase equilibrium behavior in mixtures of water + light gases, and water + heavy hydrocarbons. An extensive literature survey for experimental data of vapor–liquid and liquid–liquid equilibria on mixtures containing water has been completed. Vapor–liquid equilibrium (VLE) data are available in the literature for a number of binary mixtures of a light gas (hydrogen, methane, ethane...) in water at conditions of interest in this work. However, the liquid–liquid equilibrium (LLE) data for water + heavy hydrocarbon are rather limited. A static apparatus has been constructed for LLE measurements. Mutual solubilities were determined for six binary mixtures of water with m-cresol, quinoline, indoline, 1,2,3,4-tetrahydroquinoline, thianaphthene, or 9,10-dihydrophenanthrene at the three-phase vapor–liquid–liquid equilibrium (VLLE) pressure over the temperature range of 294 to 503 K. A cubic chain-of-rotators (CCOR) equation of state has been developed for representation of fluid-phase behavior for both nonpolar and polar substances. This equation calculates the vapor pressure of water to an accuracy of about 0.8% AAD (absolute average deviation) and liquid density to 1.5% from the triple point to the critical. The CCOR equation is extended to mixtures upon introducing mixing rules for the equation constants. We have tested the CCOR equation with the one-fluid mixing rules. The calculated results indicate that the conventional quadratic mixing rules are adequate for the representation of VLE of most water binaries. For water + hydrocarbon LLE or VLLE, the conventional mixing rules are not sufficient. New mixing rules will be developed to improve the calculations.

## Stanford University
## Stanford, California 94305

### *406. Fundamental Studies of Heat Transport, Fluid Mechanics, and Stability in Porous Media*

*G.M. Homsy* **$191,200**
*Department of Chemical Engineering* **(29 mo.)**

This project treats problems in flow and transport phenomena in porous media whose solutions are of interest in energy recovery processes. Macroscopic and microscopic problems are addressed. Our macroscopic work has focused mostly on viscously driven instabilities (fingering) that occur in displacement processes. For immiscible flows, we have discovered an intriguing tip-splitting instability of large-scale fingers that may, under some circumstances, lead to geometrically complex fractal patterns. Experimental work continues. We have recently completed a linear theory of fingering in miscible displacements that is in excellent agreement with available experiments. Current work will extend this theory to nonlinear fingering. New studies of blob dynamics in constricted-tube models of porous media have begun.

## University of Wisconsin
## Madison, Wisconsin 53706

### *407. Interphase Transport and Multistage Separations*

*W.E. Stewart* **$74,000**
*Department of Chemical Engineering*

The project goal is to provide new physical understanding of stagewise separation processes, and efficient algorithms for computer-sided engineering of these processes. The physical studies include boundary-layer scaling analysis and multicomponent transport theory; the algorithmic studies include new collocation and continuation methods. Results from the second year of research include: (1) asymptotic expansions for the spectra of scalar fluctuations in turbulent flows; (2) a comprehensive numerical study of approximation methods for prediction of multicomponent mass transfer, leading to simple, accurate reference-property rules for the linearized matrix method; and (3) extension of our collocation method for plate columns to detect liquid-phase immiscibility, and to locate the boundaries of the resulting extra phase.

# Heavy Element Chemistry

## Florida State University
## Tallahassee, Florida 32306

### *408. Research in Actinide Chemistry*
*G.R. Choppin* **$104,000**
*Department of Chemistry*

This research is concerned primarily with complexes of actinide elements. To supplement data on trivalent actinides, similar systems are investigated for trivalent lanthanides using the wider variety of techniques available with the latter elements. Our studies include measurements of the thermodynamic parameters of complexation of both inorganic and organic ligands, the kinetics of complexation, the spectroscopic properties of complexed species using electronic (f-f) transitions and nuclear magnetic resonance, and the redox properties of the actinides. Reduction of neptunium(VI) has been shown to occur via the phenolic group but not the carboxylate of hydroxybenzoic acids. Direct calorimetry with $^{248}$Cm has provided improved values for the $\Delta H$ and $\Delta S$ of complexation with acetate and EDTA. Kinetic studies of dissociation of thorium–polyelectrolyte systems have given a multiterm rate expression that varies with residence time (prior to dissociation) of thorium on the polyelectrolyte. Synthetic (polymaleic acid) and natural (humic acid) polyelectrolytes gave similar results. Calorimetric studies of the synergistic reaction of $Th^{+4}$, $UO_2^{+2}$, and $Nd^{+3}$ complexes of TTA or PMBP with TBP or TOPO have demonstrated the major role of cation dehydration in such solvent extraction systems.

## University of New Mexico
## Albuquerque, New Mexico 87131

### *409. Development of Surface Immobilized Ligands for Actinide Separations*
*R.T. Paine* **$88,000**
*Department of Chemistry*

The project objective is to develop systematic synthetic methods for the formation of new classes of organic solvent-soluble extractants and for the production of solid-state immobilized extractants suitable for selective ion chromatographic separations of metal ions present in nuclear fuel reprocessing and industrial waste solutions. In particular, fundamental investigations of steric and electronic effects that influence and modify extractant–metal ion interactions are in progress, and new flexible bifunctional and trifunctional phosphonate extractants are prepared. Isolated liquid–liquid extraction complexes of these ligands are studied at the molecular level by spectroscopic and x-ray crystallographic methods. In turn, the resulting molecular architecture data are used to design improved extractants and to model surface immobilized extractant–metal interactions. Extraction equilibria for lanthanide and actinide ions in contact with several phosphonate extractants attached to various organic and inorganic polymer backbones are measured.

## SRI International
## Menlo Park, California 94025

### *410. Chemistry of Gaseous Lower Valent Actinide Halides*
*D.L. Hildenbrand, K.H. Lau* **$89,000**
*Physical Sciences Division*

The objective of this project 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 chemical bonding and chemical reactivity in these systems can be elucidated in a systematic way. Our principal focus is on the gaseous halides, mainly the lower valent halides, since there is little or no 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. The bond dissociation energies and their variation with the number of halogen ligands yield insight into the electronic character of the bonding, while the absolute entropies provide useful checks on assigned structures and electronic partition functions. Current studies are concerned with the gaseous thorium–bromine system, the lower valent uranium and thorium oxyfluorides, and the uranium chlorobromides, and with further studies of the stability of uranium pentafluoride. A clear pattern of bond dissociation energies and electronic entropies is beginning to emerge; 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

### *411. Magnetic Measurements of the Transuranium Elements*
*S.E. Nave* **$100,000**
*Department of Physics*

A SQUID-based micromagnetic susceptometer in the facilities at the Transuranium Research Laboratory is used to measure the magnetic properties of americium, curium, berkelium, californium, and einsteinium metals and compounds. The research catalogs magnetic behavior of unmeasured heavy actinides between 4.2 K and room temperature and 0 to 5 tesla. The study provides a measure of the degree of localization of the 5f electrons and examines the effects produced by neighbor–neighbor overlap. The effective magnetic moments of heavy atoms and the observed magnetic transition temperatures (if any) are examined within the context of the intermediate coupling model. Presently the work involves a study of the magnetic properties of $CfCl_3$ as a function of crystal structure and magnetic ordering in actinide monopnictides, particularly the bismuthides.

### *412. Physical-Chemical Studies of the Transuranium Elements*
*J.R. Peterson* **$136,000**
*Department of Chemistry*

This project provides training for pre- and postdoctoral students in chemical research with the transuranium elements through continuing investigations of the basic chemical and physical properties of this group of elements and the interpretation and correlation of the results obtained. 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 relationships of metallic structures to metallic valence and radius; (3) the extent and magnitude of the actinide contraction; (4) the magnetic, thermodynamic, spectroscopic, and crystallographic properties of these materials as related to general theories; (5) the effect of self-irradiation on chemical and physical properties; (6) the chemical and physical consequences of radioactive decay in the bulk-phase solid state; and (7) in general, the range of validity of the actinide hypothesis. Research activities include: (1) spectroelectrochemical studies in aqueous and nonaqueous media; (2) measurement of heats of solution; (3) absorption and Raman spectroscopies in solution and in the solid state (the latter as a function of temperature or pressure); (4) structural changes of transuranium elements and compounds as a function of temperature or pressure; (5) direct or indirect (via radioactive decay) synthesis of compounds containing unusual oxidation states; (6) determination of the structures of einsteinium compounds; and (7) studies of the fundamental chemistry of the transeinsteinium elements.

## Stanford Synchrotron Radiation Laboratory Operation

### Stanford Synchrotron Radiation Laboratory
### Menlo Park, California 94025

*413. Stanford Synchrotron Radiation Laboratory Operation*
*A. Bienenstock* **$6,800,000**

This project supports the Laboratory's operation, making possible otherwise-funded research by users in many scientific areas. Research performed in the vacuum ultraviolet area includes: ionization properties of small molecules; structural and electronic properties of microstructures; properties of ultrathin layers and small clusters; kinetic process in laser materials; lithography and microscopy; and static properties and dynamic processes of chemisorbed gases. Research in the chemical and biological sciences includes: structure and function of homo- and heterogeneous catalysts; structure of metals; metal oxide and semiconductor surfaces and their interactions with small molecules; chemical reactivities in the gas phase; structure of general chemical compounds; multiple wavelength imaging; protein structures and functions; dynamics and fluctuations in biological systems; membrane structures and membrane–protein interactions; and structure and function of metal site in metalloproteins and metalloenzymes. X-ray physics and materials sciences research includes: structure of amorphous materials; coordination of impurities and alloying species; structures of, and phase transitions in, surfaces and thin surface layers; kinetics of structural changes in materials; phase transitions at high pressure; structure of crystalline materials; electronic structure of materials through edge absorption studies; fundamental x-ray scattering and absorption physics; and atomic physics. Accelerator, insertion device, and advanced instrumentation development for synchrotron radiation enhancement are also principal activities.

# 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 collaboration by the off-site scientist with one or more inhouse 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. Louis C. Ianniello, Acting Director of Materials Sciences, ER-13, U. S. Department of Energy, Washington, D.C. 20545.

## ATOMIC SPECTROSCOPY FACILITY

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

The Argonne spectroscopic facility is designed for high-resolution investigations of atomic and molecular optical spectra by using a unique combination of large-scale dispersive instruments with state-of-the-art holographic gratings and pulsed, sharply tunable coherent light sources for excitation energies of up to 11 eV. Photographic, Reticon array, and resonance-ionization detectors with associated data-processing equipment are available for a wide variety of experiments. Peripheral equipment includes a 50-kG superconducting magnet with a 24-inch room-temperature bore, and an automatic plate-measuring comparator. Nd-YAG laser-driven dye lasers are used with doublers and $H_2$-Raman scattering to cover the 200–850 nm range and to produce coherent radiation between 118 and 125 nm by four-wave mixing in mercury vapor.

### COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists.

### PERSON TO CONTACT FOR INFORMATION

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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 | $>10^7$ |
| 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 125 |

# 4.5-MV DYNAMITRON ACCELERATOR

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 electron spectrometers including a high-resolution, large solid-angle McPherson spherical analyzer, and (6) a large area multiwire proportional counter capable of detecting up to eight particles simultaneously with submillimeter position and subnanosecond time resolution, and (7) a post-acceleration 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

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Argonne, IL 60439

Phone:
Comm. (312) 972-4039
or FTS 972-4039

## TECHNICAL DATA

| | |
|---|---|
| Range of terminal voltages attainable | 0.3 to 4.5 MV |
| Range of ion beam currents attainable | 0.1 nA to 500 $\mu$A |
| Monatomic singly charged ion beams available | Most elements |
| Monatomic multiply charged ion beams available | Rare gases, transition metals |
| Typical molecular-ion beams available | $H_2^+, H_3^+, HeH^+, CH_n^+$ (n = 1,4), $OH_n^+$ (n = 1,3), $CO^+, O_2^+$, etc. |
| Pulse mode (post-chopper) | |
| Pulse width | 1 nsec to 10 msec |
| Repetition rate | 1 MHz to 8 MHz |

# PREMIUM COAL SAMPLE PROGRAM

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 are 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 is expected to be complete 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

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TWX 910-258-3285
USDOE-CH ARGN

# PULSE RADIOLYSIS FACILITY

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 $\mu$sec. In addition, a 5 psec pulse with the same peak current is presently being developed and is expected to be available by July, 1986. In liquids, transient concentrations up to 20 $\mu M$ can be generated with the 25-psec pulse, and concentrations in excess of 10 m$M$ 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

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Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Phone:
Comm. (312) 972-3471
or FTS 972-3471

## TECHNICAL DATA

| | | |
|---|---|---|
| Energy | | |
| Transient mode | 21 MeV | |
| Steady-state mode | 14 MeV | |
| Average current | 200 $\mu$A (maximum) | |
| Pulse repetition rate | Single pulse to 800 pps<br>(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) | |
| Pulse width | 25 ps<br>4 to 100 ns | transient mode |
| | .25 to 10 $\mu$s | steady state mode |

# ATOMIC PHYSICS AND NUCLEAR ANALYTICAL TECHNIQUES

Atomic and Applied Physics Division
Department of Applied Science
Brookhaven National Laboratory
Upton, NY 11973

The objective of this program is to make available facilities for research in atomic physics and the development and application of nuclear analytical techniques. Experiments in these fields require the availability of a wide range of ion and photon beams for maximum effectiveness. These beams cannot be provided at a single accelerator, but require the use of varied apparatus at a whole complex of accelerators. A 3.5-MV electrostatic accelerator is used primarily for experiments on nuclear analytical techniques. Notable features include a triton beam, medium resolution microprobe, rabbit system, and 200-kV ion implanter arranged for simultaneous implantation and analysis. The MP tandem accel-decel accelerator provides beams of most elements with an energy range from 2 MeV to 500 MeV. Ion charge state and ion energy can be selected over a wide range of energies using the accel-decel feature. Possible use of the tandem accelerators is determined by the needs of the relativistic heavy-ion program. Equipment for beam-foil spectroscopy and many types of ion-atom collision experiments are available. Photon beams with energies from 3 to 20 keV are provided at the National Synchrotron Light Source (NSLS). Either white or monochromatic radiation can be selected. The high brightness of the source gives unique opportunities in both atomic physics and nuclear analytical technique experiments. Extensive instrumentation is available in both areas.

## 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
Division of Atomic and Applied Physics
Department of Applied Sciences
Building 901A
Brookhaven National Laboratory
Upton, NY 11973

Phone:
Comm. (516) 282-4588
or FTS 666-4588

## TECHNICAL DATA

| | |
|---|---|
| 200-kV Ion Implanter | |
| Range of terminal voltages attainable | 20 to 200 kV |
| Range of maximum ion beam currents available | 1 to 100 $\mu$A |
| 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 100 $\mu$A |
| Ion beams available | $^1$H, $^2$H, $^3$H, $^3$He, $^4$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 $\mu$A |
| 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 | Filtered white radiation |
| Photon flux at target | $4 \times 10^7$ photons/(sec · eV · mm$^2$) at 8 keV |

# NATIONAL SYNCHROTRON LIGHT SOURCE

National Synchrotron Light Source
Brookhaven National Laboratory
Upton, NY 11973

The National Synchrotron Light Source (NSLS) facility consists of a 750-MeV storage ring for VUV and IR research and a 2.5-GeV storage ring for X-ray research. Attractive features of the synchrotron radiation include high brightness and intensity, a broad and continuous spectral range, high polarization, and pulsed time structure (subnanosecond pulses). With each of the 28 X-ray and 16 VUV beam ports being further split into from 2 to 4 beam lines, it will be possible, when NSLS becomes fully operational, to have as many as 100 experiments running simultaneously. The facility presently has a 38-period soft x-ray undulator installed on the VUV ring and a 10-period soft x-ray undulator installed on the x-ray ring. These are designed for spectroscopy and microscopy experimentation. Several further wiggler and undulator magnets are presently being designed which will significantly increase the photon intensity and brightness.

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, photoemission, radiometry, lithography, microscopy, circular dichroism, and infrared vibrational spectroscopy.

## USER MODE

The policy for experimental utilization of the NSLS is designed to enable the scientific community to cooperate in the design and fabrication of experimental apparatus. 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 (PRT's). The PRT's are given priority for up to 75% of their beam line(s) operational time for a three-year term. Research groups are now in the process of forming insertion device teams (IDT) to design and instrument beam lines and insertion devices.

General Users are able to perform experiments on an NSLS facility beam line or on a PRT beam line, which are available for use by non-PRT members for at least 25% of its total operational time. For the PRT beam lines, PRT's provide liaison and utilization support to General Users.

Proprietary research can be performed at the NSLS. A full-cost recovery fee will be charged for the amount of beam time utilized. The DOE has granted the NSLS a Class Waiver, under whose terms Proprietary Users of the NSLS will have the option to retain title to inventions that result from research performed at the NSLS.

A program is available to support faculty/student research groups performing experiments at the National Synchrotron Light Source (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

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NSLS, Bldg. 725B
Brookhaven National Laboratory
Upton, NY 11973

Phone:
Comm. (516) 282-7114
or FTS 666-7114

## TECHNICAL DATA

| Facilities | Key features | Operating characteristics |
|---|---|---|
| VUV electron storage ring | High brightness; continuous wavelength range ($\lambda > 5$ Å); 16 beam ports | 0.75-GeV electron energy |
| X-ray electron storage ring | High brightness; continuous wavelength range ($\lambda > 0.5$ Å); 28 beam ports | 2.5-GeV electron energy |

| Instruments | Key features |
|---|---|
| Monochromators | |
| Plane grating | 12 Å $< \lambda <$ 1500 Å; moderate resolution |
| Zone plate | 8 Å $< \lambda <$ 100 Å; moderate resolution |
| Toroidal grating | 10 Å $< \lambda <$ 2500 Å; high intensity; moderate and high resolution |
| Extended range grasshopper | 20 Å $< \lambda <$ 2000 Å; high resolution |
| Wadsworth | 300 Å $< \lambda <$ 3000 Å; high intensity; moderate resolution |
| Seya and Czerny-Turner | 1200 Å $< \lambda <$ 12000 Å; high intensity; moderate resolution |
| Two crystal | 0.04 Å $< \lambda <$ 2500 Å; high resolution; fixed exit beam |
| Two crystal/two grating | 2.5 Å $< \lambda <$ 2500 Å; high resolution; fixed exit beam |
| Six circle spectrometer/diffractometers | High positional and rotational accuracy |
| Experimental stations | Photoemission; magnetic circular dichroism; fluorescence; gas phase spectroscopy; microscopy; lithography; holography; EXAFS; inelastic scattering; crystallography; radiometry; topography; small angle scattering |
| Permanent magnet undulator | 100 Å $< \lambda <$ 1000 Å; high intensity and brightness |

# JAMES R. MACDONALD LABORATORY

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 magnet 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 experiments pertinent to DOE program goals.

## COLLABORATIVE USE

Users are encouraged to seek a collaborator on the staff or can submit a brief proposal.

## PERSON TO CONTACT FOR INFORMATION

Patrick Richard, Director    Phone: (913) 532-6783
James R. Macdonald Laboratory
Department of Physics
Kansas State University
Manhattan, KS 66506

## TECHNICAL DATA

### EN Tandem

| | |
|---|---|
| Beams | Most elements |
| Terminal voltages | 0.3 to 6 MV |
| Output currents | Up to 10 $\mu$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 | $ME/q^2 \leqslant 150$ |

### 3-MV Van de Graaff

| | |
|---|---|
| Beams | $^1$H or $^4$He |
| Terminal voltages | 0.3 to 3 MV |
| Output currents | Up to 100 $\mu$A |
| Repetition rate | DC only |
| Magnet limitations | None |

### 100-kV Accelerator

| | |
|---|---|
| Beams | Most elements |
| Terminal voltages | 20 to 100 kV |
| Output currents | Up to 10 $\mu$A, depending on the ion species |
| Magnet limitations | None |

# PULSE RADIOLYSIS FACILITY

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. 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.

## COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists or by a proposal to the laboratory director.

## PERSON TO CONTACT FOR INFORMATION

J. J. Bentley, Assistant Director    Phone:
Notre Dame Radiation Laboratory    Comm. (219) 239-6117
Notre Dame, IN 46556    or FTS 333-8220

### TECHNICAL DATA

| | |
|---|---|
| Electron source | 8-MeV linear accelerator |
| Operating mode | Single pulse, with signal averaging |
| Data collection | LSI-II |
| Pulse width | 5, 10, 20, 50 nsec |
| Time resolution (RC) | 2 nsec |
| Pulse current | Up to 1 A |
| Repetition frequency | 0.2 $\text{sec}^{-1}$ |

| | |
|---|---|
| Optical absorption measurements | |
| Spectral region | 210 to 750 nm |
| Sensitivity | ±0.00002 absorbance |
| Conductivity | |
| pH range | 3 to 11 |
| Sensitivity | ±5 mhos/cm |

## ELECTROMAGNETIC ISOTOPE SEPARATIONS (CALUTRON) FACILITY

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. Applications 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
Stable Isotope Enrichment
Operations Division
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Oak Ridge, TN 37831

Phone:
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or FTS 624-0425

## EN-TANDEM

Physics Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

The EN-Tandem is operated primarily as an atomic physics facility. The highest terminal voltage is 6.0 MV. The widest possible variety of ion species are available from a selection of ion sources. 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) a merged electron–heavy ion beam apparatus with a merged region ~1 meter in length; (2) an ~14-meter flight tube with the capability of doing very small angle scattering and detecting individual charge states; (3) a Penning ion trap apparatus; (4) an Elbeck magnetic spectrograph with position sensitive detectors; (5) Si(Li) detectors and a curved crystal spectrometer; (6) both low- (eV to keV) and high- (MeV) monoenergetic positron sources (being developed); (7) 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

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P.O. Box X
Oak Ridge, TN 37831

Phone:
Comm. (615) 574-4781
or FTS 624-4781

## TECHNICAL DATA

| | |
|---|---|
| Beams | Most elements |
| Terminal voltages | 0.3 to 6.0 MV |
| Source beam currents | Several hundred nA to several $\mu$A |
| Output currents | Up to 2 $\mu$A, depending on the ion species and charge state |
| Repetition rate | DC only |
| Magnet limitations | $ME/q^2 \leqslant 80$ |

# HIGH FLUX ISOTOPE REACTOR

Operations Division
Oak Ridge National Laboratory
Oak Ridge, TN 37830

The prime purpose of the High Flux Isotope Reactor (HFIR) is to make research quantities of $^{252}$Cf and other transuranium isotopes. These materials are produced in the flux trap in the center of the HFIR fuel element where a thermal-neutron flux of $3 \times 10^{15}$ neutrons/(cm$^2$ · 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 100 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 $1 \times 10^{15}$ neutrons/(cm$^2$ · 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

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Oak Ridge National Laboratory
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Oak Ridge, TN 37831

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# TRANSURANIUM PROCESSING PLANT

Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37830

The objective of this program is to supply transplutonium elements for use in research. This involves operation of the Transuranium Processing Plant (TRU), which is the production, storage, and distribution center for the DOE heavy-element research program. Target rods are fabricated at TRU, irradiated in the High Flux Isotope Reactor (HFIR), and processed at TRU for separation, recovery, and purification of the heavy actinides up through $^{257}$Fm. Since their construction in the mid-1960's, TRU 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 TRU are used nationally and internationally to study the basic physics and chemistry of the transuranium elements and, also, they are being used in research and development programs relating to environmental effects, biological effects, and waste isolation.

## PERSON TO CONTACT FOR INFORMATION

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# COMBUSTION RESEARCH FACILITY

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.) 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.

The facility is located in Livermore, California, in the San Francisco Bay area, near major universities and other U. S. Government supported laboratories.

## 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.

## PERSON TO CONTACT FOR INFORMATION

| | |
|---|---|
| Dan L. Hartley, Director<br>Combustion Research Facility<br>Sandia National Laboratory<br>Livermore, CA 94550 | Phone:<br>Comm. (415) 422-2747<br>or FTS 532-2747 |

or

| | |
|---|---|
| Peter L. Mattern, Manager<br>Combustion Sciences Department<br>Sandia National Laboratory<br>Livermore, CA 94550 | Phone:<br>Comm. (415) 422-2520<br>or FTS 532-2520 |

## TECHNICAL DATA

| Equipment | Key features |
|---|---|
| Flashlamp-pumped, tunable dye laser | Long pulse, high energy, high average power:<br>2-$\mu$sec pulse length<br>5 J/pulse, 10 Hz<br>Tunable 440 to 620 nm<br>0.03-nm bandwidth |
| Multipurpose pulsed laser system | High peak power, high resolution doubled YAG and tunable dye lasers:<br>Single mode capability<br>10 to 500 mJ/pulse<br>10 to 20 nsec/pulse |
| Low-pressure flames | 10 torr to 1 atm<br>Mass spectrometer sampling probe<br>LIF detection of radicals |
| Atmospheric flames | Diffusion and premixed flames |
| High-pressure flame | Combination of diffusion flame burner with high pressure flow chamber:<br>Pressures up to 20 atm<br>Slot- or cylindrical-geometry burner<br>2-D axisymmetric laminar diffusion flame |
| Vertical turbulent diffusion flame | Open-circuit, induced-draft wind tunnel with co-flowing axisymmetric fuel jet:<br>30- by 180-cm viewing section to 6000 scfm flow |
| Combustion bomb | Simulated constant-volume engine combustion |
| Internal combustion research engines | Highly repeatable environment for homogeneous charge and diesel combustion studies |
| Experimental diagnostics research facilities | Laser fluorescence laboratory |
| Visitor laboratory | Rayleigh, Mie, and Raman 2-D imaging |

# STANFORD SYNCHROTRON RADIATION LABORATORY

Stanford Synchrotron Radiation Laboratory
Bin 69, P.O. Box 4349
Stanford, CA 94305

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 using 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 use of synchrotron radiation.

The radiation comes from both the 4 GeV storage ring, SPEAR, and the 16 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 20 exprimental stations on 8 beam lines covering the spectrum from 6 to 45,000 eV. An undulator beam line serving three experimental stations covering the energy range 10 to 1000 eV is in the commissioning stage. The single beam line on PEP is an undulator beam line which provides the world's most brilliant photon beam at X-ray wavelengths.

## USER MODE

SSRL is currently used by approximately 550 scientists from 108 institutions in 32 states and 11 foreign countries. Access to the facility is through a refereed proposal system. Proposals are due September 1 and March 1 each year. The booklet "General Information and Proposal Guidelines" available from SSRL contains information pertinent to proposal submittal. To date 1033 proposals for research have been received. Demand for experimental time is approximately twice that which can be accommodated.

## PERSON TO CONTACT FOR INFORMATION

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Manager, User Research
Administration
SSRL
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Stanford, CA 94305

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# TECHNICAL DATA

## CHARACTERISTICS OF SSRL EXPERIMENTAL STATIONS

**SSRL presently has 20 experimental stations, 19 of which are located on SPEAR and one on PEP. Nine of these stations are based on insertion devices while the remainder use bending magnet radiation.**

| | **Horizontal angular acceptance (Mrad)** | **Mirror cutOff (KeV)** | **Monochromator** | **Energy range (eV)** | **Resolution $\Delta E/E$** | **Approximate spot size hgt × wdth (mm)** | **Dedicated instrumentation** |
|---|---|---|---|---|---|---|---|
| **Insertion Device Stations** | | | | | | | |
| Wiggler Lines–X-ray | | | | | | | |
| End stations | | | | | | | |
| IV-2 (8 pole) | | | | | | | |
| Focused | 4.6 | 10.2 | 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 | |
| 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 | |
| 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 |
| VII-3 | 1.0 | – | Double crystal | 2,800 to 45,000 | $\sim 10^{-4}$ | 2.0 × 20.0 | |
| Undulator lines–VUV soft x-ray | | | | | | | |
| V-1 | 1.5 | – | None | 10 to 1,200 | $\geq 7\%$ | 6.0 × 8.0 | Variable apertures |
| Undulator lines–x-ray | | | | | | | |
| PEP 5B | Full | 15.0 | Double crystal | 12,000 to 20,000 | $\sim 10^{-6}$ | 0.6 × 6.0 | |
| **Bending Magnet Lines** | | | | | | | |
| X-ray | | | | | | | |
| I-4 | 2.2 | | Curved crystal | 6,000 to 9,500 | ~60 eV | 0.25 × 0.5 | |
| I-5 | 1.0 | – | Double crystal | 3,800 to 29,300 | $\sim 10^{-4}$ | 2.0 × 20.0 | Area detector/CAD-4 |
| II-2 (focused) | 4.8 | 8.9 | Double crystal | 2,800 to 8,900 | $\sim 5 \times 10^{-4}$ | 2.0 × 4.0 | |
| II-3 | 1.0 | – | Double crystal | 2,800 to 30,000 | $\sim 5 \times 10^{-4}$ | 2.0 × 20.0 | |
| II-4 | 1.0 | – | None | 3,200 to 30,000 | | 4.0 × 15.0 | |
| Lifetimes port | 1.8 | – | None | 1 to 6 | Bandpass >10A | 4.0 × 0.4 | |
| VUV/Soft x-ray | | | | | | | |
| I-1 | 2.0 | | Grasshopper | 32 to 1,000 | $\Delta\lambda = 0.1$ to 0.2A | 2.0 × 1.0 | |
| I-2 | 4.0 | | Seya-Namioka | 4 to 40 | $\Delta\lambda = 0.2$ to 6A | 1.0 × 3.0 | |
| III-1 | 2.0 | | Grasshopper | 15 to 1,200 | $\Delta\lambda = 0.05$ to 2A | 1.0 × 1.0 | |
| III-3 | 8 to 10 | | Jumbo | 800 to 4,000 | 0.35 to 7 eV | 2.0 × 4.0 | |
| III-4 | 2.0 | | Multilayer | 2 to 3,000 | White or<br>$\Delta\lambda/\lambda = .3\%$ | 2.0 × 11 | Vacuum diffractometer/ exposure station |

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*Specialized portable beam line instrumentation available: VG Chamber, Perkin Elmer Chamber, CAD-4, SAS Camera.

# FY 1986 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 1986 equipment funds for Chemical Sciences programs were assigned as follows:

| Facility | Equipment funds |
|---|---|
| Ames Laboratory | $ 407,000 |
| Argonne National Laboratory | 3,571,000 |
| Brookhaven National Laboratory | 1,433,000 |
| Idaho National Engineering Laboratory | 13,000 |
| Lawrence Berkeley Laboratory | 519,000 |
| Los Alamos National Laboratory | $ 31,000 |
| Monsanto Research Corporation–Mound | 46,000 |
| Notre Dame Radiation Laboratory | 275,000 |
| Oak Ridge National Laboratory | 1,015,000 |
| Pacific Northwest Laboratory | 427,000 |
| Sandia National Laboratories, Albuquerque | 49,000 |
| Sandia National Laboratories, Livermore | 577,000 |
| Solar Energy Research Institute | 143,000 |
| Stanford Synchrotron Radiation Laboratory | 455,000 |

# INSTITUTION INDEX

# SELECTED TOPICS OF GENERAL INTEREST

# INVESTIGATOR INDEX