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# Summaries of FY 1984 Research in the Chemical Sciences

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**September 1984**

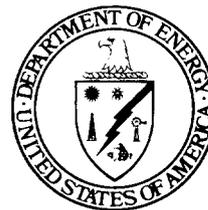
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Office of Energy Research  
Division of Chemical Sciences**

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# Summaries of FY 1984 Research in the Chemical Sciences

**September 1984**

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

This report was compiled for the Office of Energy Research project from 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 year, for the first time, this publication shows projects supported by 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 index, and the summaries themselves. Energy technologies that can be advanced by use of the basic knowledge generated in this program are provided in the index 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 summar-

ized 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 is distributed among several different kinds of performing organizations. About half the projects take place at DOE laboratories, and half take place at universities and industrial laboratories. In DOE laboratories, most of the researchers are fully engaged in this work, whereas most university and industrial researchers necessarily divide their time among duties involving this research, other research, teaching responsibilities, etc. Thus about 70% of the funding goes to Federal laboratories, 25% to the academic sector, and the remainder to industrial and nonprofit laboratories.

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.

**Elliot S. Pierce, 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**

**OFFICE OF THE DIVISION DIRECTOR**

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**Atomic Physics**

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\*On leave from Lehigh University.

†On leave from Brigham Young 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 (01- )**

### **Photochemical and Radiation Sciences (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 (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 biomolecular 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; advanced diagnostic methods, 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 (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, momentum, and matter. These studies strive to obtain the best and most complete fundamental knowledge of the properties and interactions of photons, electrons, atoms,

ions, and simple molecules. Continued emphasis of this research has been 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 located at upper energy levels. The study of processes that lead to the production of coherent radiation and of the statistical properties of this radiation as they modify elementary atomic physics processes also constitute part of this program.

## **Processes and Techniques Branch (02- )**

### **Chemical Energy (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 (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 (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 on pages 88 and 89 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 the DOE Nuclear Energy Technology program 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 point 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.

## 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

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# Summaries of FY 1984 Research Administered by Chemical Sciences

## NATIONAL LABORATORIES

### Heavy Element Chemistry

**Argonne National Laboratory**  
Argonne, Illinois 60439

**Division of Chemistry** **\$1,300,000**

1. **Heavy Element Chemistry Research**  
*W.T. Carnall, J.V. Beitz, H.M. Crosswhite, L.R. Morss, J.C. Sullivan*

The objective of this program is to advance the chemistry and physics of the actinide elements consistent with the energy development goals of the Department of Energy. Laser spectroscopy and photophysics efforts explore and interpret the unique electronic structure of the actinides, while efforts in photochemistry and inorganic fluorine chemistry interact to develop novel processes for chemical and isotope separations utilizing high-valency reactive species of Np, Pu, and Am. Parallel research on Cm, Bk, Cf, and Es compounds extends the understanding of electronic structure and chemical properties of the heaviest elements. Solid state and organometallic research activities characterize new transuranium compounds, especially in low and high oxidation states, and systematize bonding and reactivity patterns throughout the series. Comparison with the chemistry of both the transition and rare earth elements is stressed, and emphasis is placed on the use of thermochemical methods. Oxidation-reduction and complex formation reactions of actinides in solution are investigated with pulse radiolysis, stopped-flow, NMR and thermodynamic methods in order to interpret and predict the behavior of these elements in modern process chemistry, as well as in the aqueous environment. [10.9 FTE]

**Lawrence Berkeley Laboratory**  
Berkeley, California 94720

**Materials and Molecular Research** **\$1,230,000**  
**Division**

2. **Actinide Chemistry**  
*N.M. Edelstein*

The purpose of this program is to study actinide materials in order to provide the basic knowledge necessary for their safe and

economic utilization in present and future technology. The work includes the 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 with which to design new synthetic schemes to produce new materials. A major aspect of the program 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. Applications of new spectroscopic techniques for characterization of actinide species in solution are being undertaken. [15.0 FTE]

**Los Alamos National Laboratory**  
Los Alamos, New Mexico 87544

**Isotope and Nuclear Chemistry Division** **\$260,000**

3. **Actinide Valence, Host, and Radiation Effects**  
*P.G. Eller*

There is only sparse information regarding valence stabilities of the transuranium elements Pu, Am, and Cm in solids important to nuclear waste storage. We are determining the effects of ion size and radiation on actinide valence stabilities and site selectivities, particularly of Am(III, IV) in selected oxide matrices. Since Pu, Am, and Cm have profoundly different aqueous valence stabilities, we anticipate stability differences when they are incorporated in solids and exposed to radiation (self radiation or other). We have developed an approach to predicting actinide valence stabilities and site selectivities in solids and are determining the validity of the hypothesis by synthesizing and studying appropriate actinide materials by spectroscopic and diffraction techniques. We also continue appropriate solid state and solution characterization of oxo and fluoride species (e.g.,

MO<sub>2</sub><sup>+</sup>, MOF<sub>4</sub>, and so forth). In addition to the obvious relevance to practical nuclear waste storage considerations, the work will also contribute to the general physico-chemical understanding of actinide behavior in condensed phase systems where oxygen is the coordinating ligand, either as free oxide ion, or when connected to another element (e.g., Si, P, and so forth). A major new initiative is exploring the applicability of Raman/resonance Raman techniques to the above materials. [0.9 FTE]

**4. Actinide Chemistry in Near-Neutral Solutions**  
*T.W. Newton, D.E. Hobart*

We are investigating a spectrophotometric method for determining the carbonate complexes of Pu(IV) and their association quotients. The method involves competition between citrate and carbonate ligands for the plutonium. Values for the formation quotients for the citrate complexes are available in the literature, but will be checked for applicability under our experimental conditions. The experiments are done on solutions saturated with argon containing known partial pressures of CO<sub>2</sub> in order to fix the thermodynamic activities of CO<sub>2</sub> and H<sub>2</sub>CO<sub>3</sub>. Preliminary experiments have shown that significant spectral changes occur when the pH is changed at constant citrate concentrations and when the citrate/bicarbonate ratio is changed at essentially constant pH. Measurements on solutions where each contains no citrate but has a different pH and constant CO<sub>2</sub> pressure indicate the presence of at least three carbonate-containing complexes in the pH range from 7 to 9.5. One or more of these may be hydroxo- or bicarbonate complexes. Spectral data are taken at 10 wavelengths between 400 and 700 nm. A non-linear least-squares program is being adapted for the quantitative interpretation of the data. [0.9 FTE]

**Materials Science and Technology Division** **\$115,000**

**5. Thermodynamics of the Transplutonium Elements and Early Actinides**  
*P.D. Kleinschmidt, J.W. Ward*

Fundamental thermodynamic data are obtained on actinide elements, compounds, and alloys by using high temperature mass spectrometry and target collection techniques. The sublimation pressures of the pure metals actinium, protactinium, and promethium are being measured. The cohesive energy is derived from these numbers and is correlated with the electronic structure of these elements. From vapor composition measurements on the americium and protactinium oxides and plutonium fluorides, the entropy and enthalpy of sublimation are determined as well as the bond dissociation energies of the gas phase molecules. The actinide series is the only one in which f electrons participate in bonding, and the effect of this is to produce unique structures and compounds. These numbers will provide a data base for any study involving transplutonium elements and compounds. Fast breeder reactor technology will require such information, as will waste storage and disposal studies. [0.8 FTE]

**Oak Ridge National Laboratory**  
**Oak Ridge, Tennessee 37831**

**Chemistry Division** **\$1,225,000**

**6. Chemistry of Transuranium Elements and Compounds**  
*O.L. Keller, C.E. Bamberger, G.M. Begun, J.K. Gibson, R.L. Hahn*

The program emphasizes the role of 5f electrons and of relativistic effects in determining the chemical and physical behavior of the actinides. Fundamental studies include: (1) investigation of the changes in 5f bonding characteristics in actinide metals and compounds as a function of pressure (up to 57 GPa); (2) derivation of thermodynamic properties of metals and compounds from high temperature Knudsen cell/mass spectrometer measurements; and (3) the determination of hydration and complexation phenomena by neutron and (synchrotron) x-ray diffraction. Also, studies are conducted on high temperature synthesis of actinide compounds which may be of interest to their immobilization in solid crystalline hosts. A new direction is being developed as a result of recent renewed interest in proposed studies of the chemistry of element 103, Lr, the last of the 5f electron series, and of the transactinide elements, in which the 7s, 7p, and 6d electrons are important. These elements could be produced in relatively large yields at accelerators using an ~40 microgram target of <sup>254</sup>Es, if the necessary financial support is obtained. Currently, the chemical identification of Lr and the determination of the radius of the 3+ ion is being carried out on the basis of 20 atoms per bombardment using a 3μg <sup>254</sup>Es target. [10.4 FTE]

**Photochemical and Radiation Sciences**

**Ames Laboratory**  
**Ames, Iowa 50011**

**Division of Fundamental Interactions** **\$270,000**

**7. Laser Spectroscopy and Electron Energy Transfer of Light Conversion Systems**  
*G.J. Small*

This project centers on the structural organization and intermolecular interactions of pigments in artificial and naturally occurring photosynthetic aggregates and the utilization of efficient electronic energy transport in biomimetic chromophoric polymers in solar energy conversion. A variety of laser spectroscopies are utilized (e.g., optical hole burning, fluorescence line narrowing, picosecond spectroscopy). In addition, nonlinear laser spectroscopies are used to study coherent unidirectional energy transfer and the vibrational structure of molecular solids. [2.48 FTE]

**8. Picosecond Spectroscopy and Reaction Dynamics**  
*W.S. Struve*

This work concerns kinetic studies of organic redox photoreactions of species attached to semiconductor surfaces using picosecond fluorescence, absorption, and photocurrent transients. Measurements of excitation transport and trapping of dyes on surfaces and electron transfer from dyes into semiconductors are made using fluorescence spectroscopy. Mechanisms of vibrational energy transfer of large molecules in solution and gas phase are determined as well as photodissociation processes. [2.75 FTE]

**Argonne National Laboratory**  
Argonne, Illinois 60439

Division of Chemistry

\$4,134,000

**9. Preparation of Organisms, Photosynthetic Pigments, and Biological Materials of Unusual Isotopic Composition**  
*H.L. Crespi, J.J. Katz, J.R. Norris, M. Wasielewski*

This program has as its objective the production of photosynthetic microorganisms substituted with biologically important stable isotopes. The major effort is in the production of fully deuterated organisms, but in addition, the Argonne National Laboratory (ANL) Chemistry Division is able to grow organisms in which non-magnetic  $^{12}\text{C}$  is replaced by magnetic  $^{13}\text{C}$ ,  $^{14}\text{N}$  by  $^{15}\text{N}$ ,  $^{16}\text{O}$  by  $^{17}\text{O}$  or  $^{18}\text{O}$ , and  $^{24}\text{Mg}$  by  $^{25}\text{Mg}$ . Large quantities of green algae, blue-green algae, and photosynthetic bacteria are routinely available in unnatural isotopic composition involving either single or multiple substitution. These organisms, and the compounds obtainable from them, have important applications in magnetic resonance spectroscopies, small-angle neutron scattering, and resonance Raman spectroscopy. Typical areas of interest are applications in the study of chlorophyll, photosynthesis, biomimetic photochemistry, and bacteriorhodopsin. Of particular importance is the ability to provide material for the growth of single crystals that contain unusual isotopes. [1.0 FTE]

**10. Gas-Phase Radiation Chemistry and Photochemistry**  
*C.D. Jonah, W.A. Mulac, A.D. Trifunac, D.B. McDonald, M.C. Sauer, Jr.*

In this program, rate constants for simple free radical reactions are being measured, many of which are of great importance in atmospheric and combustion chemistry. The pulse radiolysis technique makes it possible to measure the kinetics at pressures of one atmosphere and above and over the temperature range of  $50^\circ\text{C}$  to  $1000^\circ\text{C}$ , a range no other single experimental technique can easily span. The reaction rates of OH and OD radicals with CO and simple organic compounds are under investigation. 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. [3.3 FTE]

**11. Chlorophyll and Photosynthesis Research**  
*J.J. Katz, J.C. Hindman*

The principal objective of this research is to acquire sufficient knowledge about chlorophyll function in natural photosynthesis to make possible ultimately the replication of the natural primary light conversion event outside the living cell. Current research focuses on: (1) laser photochemistry and photophysics of chlorophyll and chlorophyll model systems; (2) new methods for the synthesis of chlorophyll and bacteriochlorophyll model systems; (3) characterization of a new chlorophyll from a recently discovered photosynthetic bacterium, *Heliobacterium chlorum*; (4) applications of californium-252 plasma desorption mass spectroscopy and high performance liquid chromatography to chlorophyll compounds and model systems; (5) structural studies by small angle neutron scattering of chlorophyll aggregates

and natural photoreaction centers; and (6) possible homologies between bioluminescent bacteria and dinoflagellates and photosynthetic organisms. [3.6 FTE]

**12. Electron Transfer and Energy Conversion and Storage**  
*J.R. Miller, D. Meisel, K.H. Schmidt, M.C. Thurnauer, W. Mulac*

This program is directed at the fundamental understanding of electron transfer between molecules held apart at fixed distances and the study of chemical mechanisms involved in the conversion and storage of light energy. Electron transfer rates are measured by pulse radiolysis of solids or compounds containing two functional groups separated by rigid molecular spacers to determine the effects of distance, energy, and molecular structure. The work on energy conversion and storage utilizes various microenvironments (1) to enhance charge separation and thus the efficiency of photoelectron transfer, and (2) to increase the yield of photo-redox products while minimizing the rates of back reactions. Particular attention is given to mechanistic studies of catalytic water-splitting in colloidal systems and in microenvironments such as micelles, polyelectrolytes, and membranes. [8.1 FTE]

**13. Physicochemical Investigations of Photosynthesis**  
*J. Norris, M. Wasielewski, M. Bowman*

The goal of this research is to elucidate the molecular mechanisms whereby light energy is converted into chemical charge separation. Natural photoreaction centers are investigated in detail so that efficient model systems can be constructed. Emphasis is placed on the determination of the structural arrangement during the natural photosynthetic charge separation process for duplication in artificial photosynthesis. Time-domain spectroscopy is used to measure distances, orientations and dynamics within the molecular components which participate in the transfer of electrons. Electron transfer events that occur in the range of a few picoseconds and longer are probed by optical and magnetic techniques. Magnetic methods and theory are developed specifically to characterize picosecond charge separation in chemical systems. Charge separation in single crystals of the reaction centers of several photosynthetic bacteria is also a subject of investigation by means of magnetic and optical spectroscopy as well as x-ray and neutron diffraction. [5.1 FTE]

**14. Radiation Chemistry and Photochemistry in Condensed Phases**  
*A.D. Trifunac, C.D. Jonah, M.C. Sauer, Jr., S. Gordon, K.H. Schmidt*

The objective of this program is the study of chemical and physical processes that follow ionization (or photoionization) in both polar and nonpolar liquids. This is relevant to radiation chemistry, for the understanding of breakdown in dielectric liquids, and for the understanding of charge separation, recombination, and transfer, phenomena which are the basis of chemical and biological processes of energy storage and utilization. Various methods of radiation chemistry and photochemistry are used to provide details of the nature and dynamics of the early transient species and their chemical fates. This includes the study of electrons and positive ions, radical ions and excited states, and the subsequent fragmentation of the excited species into radicals and molecular species. Spin dynamics in radicals and radical

ions is being used to provide better understanding of reaction kinetics. Essential tools used in this program 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. [15.3 FTE]

**15. Artificial Photosynthesis**  
*M. Wasielewski, J.R. Norris*

The goal of artificial photosynthesis research is the development of molecular systems in the laboratory that not only mimic but improve upon natural photosynthetic energy conversion. This work focuses on several interrelated facets of this problem. First, a molecular design project involves the synthesis of molecular models of the natural energy conversion system. These models, through their mimicry of features of natural photosynthesis, aid in the structural and mechanistic understanding of the natural process. Second, the photophysics and photochemistry of these systems are studied with emphasis on light-induced electron transfer reactions. Advanced spectroscopic techniques such as picosecond spectroscopy and time-domain magnetic resonance are used to study these ultrafast processes. Third, the primary photosynthetic processes themselves are being investigated with a view toward integrating the information obtained from the laboratory systems with new knowledge of natural photosynthesis. [3.2 FTE]

**Brookhaven National Laboratory**  
**Upton, New York 11973**

**Dept. of Applied Sciences** **\$1,120,000**

**16. Porphyrin Chemistry**  
*J. Fajer*

This program addresses the function of chlorophylls in the photosynthetic transduction of light into chemical energy, the catalytic role of porphyrins in bioenergetic enzymic reactions, and the application of these reactions to synthetic multi-electron photocatalysts for the fixation of carbon and nitrogen, and the decomposition of water. The work encompasses synthetic, structural, physical, and theoretical chemistry and presently includes: (1) the storage and transfer pathways of oxidizing equivalents in peroxidases and photosystem II; (2) the six-electron reduction of nitrite to ammonia mediated by isobacteriochlorins; (3) theoretical and experimental modeling of environmental effects (ligands, charges, Schiff bases, conformations) on the properties of porphyrin and chlorophyll radicals; and (4) x-ray and neutron studies of bacteriochlorins and chlorobium chlorophylls as models for exciton and electron migration, and self-assembled aggregates of these chlorophylls as models of the light harvesting antenna of green and brown photosynthetic bacteria. [6.6 FTE]

**17. Electrochemistry and Photoelectrochemistry**  
*S. Feldberg, T. Skotheim*

The objective of this program is the understanding of a variety of electrochemical and photoelectrochemical phenomena. Areas of interest comprise both theory and experiment. Theoretical studies comprise (1) analysis of the effect of picosecond irradiations of semiconductor systems (elucidation of factors affecting bulk and surface electron-hole recombination), (2) analysis of

the electrochemical switching of conducting polymers (faradaic and capacitive processes are shown to be inseparable—seemingly anomalous data obtained for chemical switching can now be shown to be consistent with electrochemical data), and (3) analysis of the underlying phenomena of diffusion and conductance in redox polymers (random walk and percolation analysis relate fundamental electron transfer kinetics to diffusion and/or conductivity). Experimental studies comprise (1) investigations of photoelectrochemical cells utilizing junctions between polypyrrole coated semiconductors and poly-(ethylene oxide) doped with KI/I<sub>2</sub>, a solvent free solid polymer electrolyte, (2) investigations of the use of doped poly-(ethylene oxide) in electrochemical cells compatible with the ultra high vacuum required by spectroscopic techniques such as ESCA, SEXAFS, and NEXAFS, (3) investigations of modified polypyrrole films incorporating redox species (e.g., phthalocyanines, ferrocene) to catalyze various electron transfer processes such as O<sub>2</sub> reduction, and (4) investigation of the spectro-electrochemistry of polypyrrole to elucidate the mechanism of electrochemical switching. [3.2 FTE]

**18. Chemical Properties and Reactions of Mono- and Dinuclear Ferrocene Derivatives**  
*M. Hillman*

This program is an investigation of the preparation and properties of metallocenes and related compounds that are expected to have application in the energy program, especially toward the splitting of water. Particularly, for the oxidation of water, ferrocene derivatives with potentials high enough to oxidize water under neutral or slightly acid conditions are required. Preparation of compounds with these properties are under way. For the reduction of water, the mechanics of the generation of hydrogen from [1.1]ferrocenophanes with strong acids is under study. Rates for hydrogen formation have been determined for three ferrocenophanes. These results indicate that the orientation of the protons on the iron atoms is a significant condition for the reaction. An understanding of this reaction will enable further modifications of the ferrocenophane so that hydrogen may be obtainable from weak acids, perhaps even water. [3.5 FTE]

**Dept. of Chemistry** **\$2,790,000**

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

This program uses pulse radiolysis and photolysis to study the behavior of transient chemical species. Principal areas of investigation are: (1) properties and reactions of electrons in dielectric fluids; (2) photoionization in dielectric fluids; (3) formation and reactions of transition metal ion complexes in unusual oxidation states; (4) the nature of transition metal ion-hydroperoxyl radical complexes; and (5) other reactions of the hydroperoxyl radical. The studies of electrons in dielectric fluids are of prime importance in understanding the basic processes of radiation chemistry, in the development of new detectors for high energy physics and for EXAFS measurements, and in controlling dielectric breakdown in transformers. The studies of transition metal complexes and hydroperoxyl radical reactions are important in developing and understanding certain homogeneous catalysis systems and methods of chemical storage of solar energy. [7.5 FTE]

**20. Photochemical Energy Conversion and Solution Kinetics***N. Sutin, C. Creutz, T.L. Netzel*

Transition metal complexes strongly absorb visible light and readily undergo electron-transfer reactions. They are excellent mediators of outer-sphere light-induced redox reactions, many of which effect net storage of the light energy and can also provide homogeneous catalytic routes for the thermal and photochemical formation of H<sub>2</sub> or the reduction of CO<sub>2</sub>. This program covers fundamental studies of the reactions of both excited-state and ground-state complexes. Since efficient light conversion and storage require the diversion of a significant fraction of the electronically excited molecules into useful reactions which must be driven in competition with rapid physical deactivation processes (luminescence and radiationless decay) and chemical back-reactions, a major project objective is the quantitative study of these physical and chemical deactivation processes. In addition, because the overall efficiency of the conversion sequence may be limited by the nature and rate of the subsequent chemical steps, mechanistic studies of the reactions of transition metal ions in high and low oxidation states are being conducted. [10.4 FTE]

**21. Energy Transfer in Chemical Kinetics***R.E. Weston, J.M. Preses*

Chemical reaction rates depend strongly on the distribution of reactant energy among translational, rotational, vibrational, and electronic degrees of freedom. Conversely, the energy distribution in reaction products provides a sensitive probe of the reaction dynamics. Collisional energy transfer plays an important role in the reaction mechanism as a process by which energetic species are produced or removed. In this program, the transfer of translational, vibrational, or electronic energy is being studied. Atoms or molecules are produced in excited states by a pulse of ultraviolet, visible, or infrared radiation. The time-dependent disappearance of these excited species is monitored by the detection of radiation, either from the parent species or from molecules that have been excited by collisional energy transfer. This program also supports both in-house research and assistance to outside users at the Dynamic Spectroscopy Beamline on the VUV ring of the National Synchrotron Light Source. [5.7 FTE]

**22. Chemistry of Energetic and Transient Species in the Gas Phase and on Surfaces***A.P. Wolf, R.A. Ferrieri*

This program investigates the basic chemistry of atomic and molecular species in neutral or charged states possessing electronic and translational excitation. Included are studies of the reactive intermediates produced by nuclear processes in the gas-phase and of the reaction pathways available to C, N, O, and halogen atoms during atom-molecule encounters. New methods of atomic species generation will use synchrotron light to produce concentrations of molecular ions high enough to allow standard instrumental analysis of the final products. The Chemistry Department mass separator will be used to produce intense beams of charged ions and atoms of oxygen and nitrogen, for reaction with hydrocarbons and other compounds. A second effort of this program uses cyclotron-generated radionuclides in catalyst research, permitting studies to be performed at femtomolar concentrations. [5.7 FTE]

**National Synchrotron Light Source****\$4,470,000****23. National Synchrotron Light Source Operations and Development***M. Blume*

The objective of this program is to support operations and development of the National Synchrotron Light Source (NSLS). The operations aspect covers: (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 VUV and X-ray storage rings; and (3) the technical support of experimental users. Development of the NSLS encompasses the 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 VUV 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 new facility. This research and development effort also provides information which will support the construction of the beam lines and devices to be funded under the Phase II construction project. [49.5 FTE]

**Lawrence Berkeley Laboratory  
Berkeley, California 94720****Chemical Biodynamics Division****\$920,000****24. Artificial Photosynthesis***M. Calvin, J.W. Otvos*

We are seeking to devise a synthetic system to accomplish a photoinduced electron transfer across phase boundaries, the way natural chloroplasts convert light into chemical energy. We have demonstrated the transfer of electrons across the lipid walls of vesicles. Other types of charged, single surfaces such as SiO<sub>2</sub> colloid have been found to increase the reaction yield when a primary reaction product is electrostatically prevented from back-reacting. We have shown that polymeric sulfonates can also produce this result. Presently, we focus on the catalysts which will be required at both the oxidation and reduction ends to produce the final products (e.g., hydrogen and oxygen). An iron-sulfur cluster has produced hydrogen electrochemically, but not yet photochemically. Certain cobalt complexes can be photochemically reduced to produce hydrogen. On the oxidation side, the natural catalyst is a manganese compound of unknown structure. We have shown that a manganese III porphyrin in a suitable microenvironment can be electrochemically oxidized to produce MnII and O<sub>2</sub>. The next step is to perform the same reaction photochemically. [6.0 FTE]

**25. Picosecond Photochemistry***J.H. Clark*

Proton-transfer and electron-transfer reactions of electronically excited molecules form the basis for virtually all existing and proposed methods for the photochemical fixation of solar energy. In this research, the techniques of picosecond laser spec-

troscopy are used to directly monitor, in real time, the dynamics of these ultrafast processes. Such studies provide insight into the details of the mechanism and kinetics of these reactions at the molecular level. This work has shown that the naphthols, substituted naphthols, and substituted phenols provide prototypical systems in which the dynamics of excited-state proton-transfer are exquisitely sensitive to subtle chemical changes. The effects of solvent environment, intermolecular and intramolecular hydrogen bonding, molecular conformation, and reactant geometry are being studied with the aim of quantifying their role in excited-state proton-transfer processes. Picosecond time-resolved resonance Raman spectroscopy and time-resolved emission spectroscopy are being carried out on a number of electronically excited organometallic complexes to establish the changes in geometrical and electronic structures which occur upon photoexcitation. Picosecond dynamic photoselection spectroscopy has been developed and is being used to probe the symmetries of the excited electronic states of large molecules in solution. [2.7 FTE]

**26. Photon Conversion**  
*G.C. Pimentel, H. Frei*

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  $O_2(^1\Delta_g)$ ,  $Hg(^3P_1$  and  $^1P_1)$ , and  $NH(^1\Delta$  and  $X^3\Sigma^-)$  with various unsaturated compounds. The reaction between imidogen and dimethylacetylene provides various isomeric products and an interesting system for hypersurface mapping. Energy storage using near infrared light, photochromism, and hypersurface mapping are goals. Temporal aspects of electronically excited transient intermediates are examined using nanosecond infrared spectroscopy. [6.0 FTE]

**Materials and Molecular Research Division** **\$470,000**

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

This project is equally interested in fundamental physical-chemical studies of small molecules and in obtaining useful atmospheric data. Laboratory studies are carried out to obtain optical cross-sections, quantum yields, infrared line shapes and absolute intensities, pressure-broadening coefficients, information about microscopic states, and macroscopic rate coefficients for molecules and reactions currently important toward interpreting atmospheric observations. The experimental methods include visible and ultraviolet laser flash photolysis, laser resonance absorption, resonance fluorescence, and infrared diode lasers. Theoretical methods include some molecular quantum mechanics and some numerical atmospheric modeling. This research has applications to problems of atmospheric ozone, and recently it has become apparent that this field of research is applicable to the role of gases other than carbon dioxide on the "greenhouse effect." [4.6 FTE]

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

This project explores photocatalyzed chemical reactions that take place at the solid-liquid interface. These reactions include the photodissociation of water to produce hydrogen and oxygen and the photon-assisted reactions of carbon dioxide and water to produce simple hydrocarbons (photosynthesis). The purpose is to explore the mechanism of photon-assisted surface reactions and then to establish the optimum conditions (of surface structure, composition, temperature, and reactant mixture) to maximize the rate of production of the desired chemicals (hydrogen and/or hydrocarbons). The materials being used include iron oxides, silicates, and sulfides of rhenium and molybdenum. [3.0 FTE]

**Notre Dame Radiation Laboratory**  
**Notre Dame, Indiana 46556**

**\$2,835,000**

**29. Theoretical Studies On Reacting Systems**  
*D.M. Chipman, J.J. Kozak, W.M. Huo*

Quantum and statistical mechanics methods are being developed to interpret phenomena in radiation chemistry and photochemistry, especially those involved in chemical-dynamic processes related to energy storage and transfer. A comprehensive statistical mechanical theory of photo- and radiation-induced redox reactions in organized molecular assemblies, such as monolayers and micelles, is being developed. These latter studies have considerable relevance to our understanding of experiments in which organizes may be applied in photochemical processes to effect the storage of solar energy. New quantum mechanical methods to perform and analyze electronic structure calculations on molecules and transient free radicals are being developed and used in conjunction with existing methods to study microscopic properties, such as molecular structures, potential energy surfaces, reaction mechanisms, photochemical properties, intermolecular forces, electron-solvent interactions, spin density distributions, and various spectroscopic parameters of molecules. Quantum dynamical aspects of the interaction of radiation with matter, specifically the temporal decay of excited states of two- and three-level atomic and molecular systems, are being studied using new analytical techniques. [11.0 FTE]

**30. Organic Photochemical Processes**  
*P.K. Das*

Nanosecond laser flash photolysis experiments are being carried out to examine the role of intermediates (radicals, biradicals, singlet and triplet states, exciplexes, and ion pairs) on the photochemical reactions of organic systems in solution. Included are studies of addition, fragmentation, hydrogen abstraction and electron transfer reactions, intermolecular energy transfer between quasi-isoenergetic triplets, intramolecular transfer in molecules containing two chromophores, electron exchange interactions with stable radicals, energy hopping along a polymeric chain and energy trapping in copolymers containing several types of chromophores. Model systems being investigated include phenyl substituted polyenes and polynes containing heteroatoms, aromatic hydrocarbons and carbonyl compounds,

small ring heterocyclic systems, stilbene analogues and polymers containing carbonyl groups. The studies on energy migration in polymers are particularly relevant to photosynthesis and to possibilities for enhancing the properties of polymers toward photodegradation or photostabilization. Programmatic emphasis is on obtaining mechanistic details of photochemically induced reactions. [8.0 FTE]

### 31. *Inorganic Photochemical Studies* *G. Ferraudi*

The photochemical properties of coordination complexes of the first and second row transition metal ions with macrocyclic and olefinic ligands are being investigated. Conventional laser flash photolysis methods are used and supplemented by product analysis. A sequential biphotonic excitation technique is also being used for probing the time and energy relationships between long-lived excited states. This research is carried out with compounds that exhibit either a direct or sensitized photochemical redox reactivity for excitation in the visible region of the spectrum and are, therefore, candidates for use in solar energy conversion. Two families of compounds are the main targets of these studies: complexes with macrocyclic ligands, namely phthalocyanines and more simple macrocycles, and metallocenes. Elucidation of general relationships between photoreactivity and the molecular structure of the macrocycles and the study of mechanisms which exhibit potential application as photocatalytic systems are essential goals of this project. [8.5 FTE]

### 32. *Microwave Studies On Radiation Chemically Produced Intermediates* *R.W. Fessenden*

Electron spin resonance (ESR) spectroscopy is being used to study radical structures, radical reaction mechanisms and kinetics, and the nature of electron spin interactions in fluids. Continuous *in situ* radiolysis generates radicals for characterization of their geometric and electronic structures by means of the observed ESR hyperfine patterns. The identity of the radicals produced and any subsequent transformations observed provide information on reaction mechanisms. Time-resolved experiments on radicals produced by pulse radiolysis measure reaction rates for intramolecular rearrangements and bimolecular disappearance, as well as rates of bimolecular spin relaxation and the extent of signal enhancement by chemically induced dynamic electron spin polarization. The latter quantities, taken together with reaction rates, provide very detailed information on reaction mechanisms in liquids. Pulsed microwave experiments, including the use of saturation recovery and electron spin echo techniques, provide information on relaxation times in a more direct way. The spin echo method also allows improved time resolution for fast reaction rate measurements. Microwave methods are also used to study electron attachment processes in high pressure gases and liquids. [6.5 FTE]

### 33. *Time-Resolved Studies of Photolytic Reactions* *R.W. Fessenden*

Time-resolved microwave absorption methods are applied to characterize the charge distribution in intermediates produced by laser excitation. Particular attention is being given to measuring the dipole moments (i.e., the degree of charge separation) in various radicals, excited states, and exciplexes that are intermediates in photochemical processes. Parallel optical experiments employing two lasers, one to form and the second to pho-

tolyse the intermediate states, are also being carried out. Applications are directed toward characterizing the various absorption bands of the intermediates in terms of their photochemical activity. Optical absorption spectroscopy is used for diagnosis. Where dissociation is observed, studies of the recombination kinetics of the resultant fragments often provide rate data not directly available. Two-pulse experiments involving laser photolysis and pulse radiolysis are also used to investigate photochemical activity of radiation chemical intermediates and reactivity of photoexcited states with radicals. These investigations are complimented by both steady-state and time-resolved ESR studies of photolytically produced radicals. [5.5 FTE]

### 34. *Theoretical Aspects of Radiation Chemistry* *K. Funabashi, A. Mozumder*

These studies relate to the physical and chemical behavior of the electron in its various aspects and in different phases. Attention is focused on the development of a unified theoretical framework capable of describing the various physico-chemical properties of solvated electrons such as their optical absorption spectra and transport properties. Problems associated with thermalization of radiation produced electrons in both gases and liquids are addressed to elucidate the nature and properties of reactions at early times, especially as they apply to track effects. Contributions of secondary electrons to the reactions within heavy particle tracks are being examined. The thermalization studies are being extended to examination of the time evolution of the effective electron temperature in molecular gases based on experimentally available elastic and inelastic cross-sections. Conclusions from these various studies are important both to many aspects of radiation chemistry and to applications where ions are important in, for example, fluorescence detectors and solid-state devices. [3.0 FTE]

### 35. *Spectroscopy of Reaction Intermediates* *J. Hardwick*

Laser-excited fluorescence, chemiluminescence, and laser intracavity absorption spectroscopy are being used to carry out high resolution spectroscopic studies of small molecules, free radicals, and molecular ions in the gas phase. These spectra yield information essential for the accurate monitoring and identification of some of the highly reactive species found in flames, as well as aiding in the prediction of their reactivity based on energetic and symmetry considerations. High-lying vibrational levels of molecules ranging in size from diatomic to small aromatic molecules are being studied at rotational resolution in their ground and excited electronic states through their optical spectra. Collisional transfer of rotational, vibrational, and electronic energy is being investigated in small molecules to aid in the development of qualitative and quantitative descriptions of the pathways by which electronic energy is thermalized in such diverse systems as flames, electric discharges, and gas lasers. [2.0 FTE]

### 36. *Photochemical Processes Following Core Electron Excitation* *R.G. Hayes*

Photochemical processes which follow excitation of 1s electrons in molecules containing several different first-row elements are being examined to determine the dependence of the photochemical processes on the specific atom which is excited. Initial efforts involve an examination of ionic photofragmentation pro-

cesses in molecules such as formamide (HCONH<sub>2</sub>) in which three distinct sites can be excited selectively. The experimental work is being carried out at the National Synchrotron Light Source using photons in the 200-500 eV region. The pathways of fragmentation are determined by the ionic electronic states left behind when the 1s holes decay by Auger processes. The distribution of these states depends on the atom which is excited initially. Thus, computational work on the valence Auger spectra of molecules, using the MS-X $\alpha$  technique, is being carried out as well. [1.5 FTE]

**37. Influence of Ordered Molecular Assemblies On Chemical Processes**

*L.K. Patterson*

These studies are directed toward developing a better understanding of the relationships between structure in organized molecular assemblies and the influence these assemblies may exert on kinetic behavior in bulk phase, assembly pseudophase, or at interfacial boundaries. A variety of unique properties has been observed for systems in which such assemblies—micelles, vesicles, spread monolayers and liquid crystals—are formed. Such properties under study include compartmentalization of reaction into microregions with well defined boundaries, non-homogeneous distribution of reactants, surface orientation of reactant molecules, surface charge effects, and reduction in dimensionality of the reactant phase. Alterations in rates and reaction mechanisms that are observed in such assemblies strongly suggest the possibility for kinetic control over a variety of photochemical and radiation chemical processes not possible in homogeneous solution. Principal attention is now directed toward studies in spread monolayers because these latter assemblies provide for significant control in the degree of organization which may be imposed on a reaction system. Investigations are being carried out also on photophysical behavior in liquid crystals which exhibit phases of varying organization. [8.0 FTE]

**38. Radiation Chemistry Data Center**

*A.B. Ross, W.P. Helman, G. Hug, I. Carmichael*

The Radiation Chemistry Data Center (RCDC) maintains and continuously updates a bibliographic data base on radiation chemistry and photochemistry and provides a variety of information services to the scientific community. Retrospective searches are carried out and bibliographies on specific topics are prepared and made widely available. A current-awareness publication, *Biweekly List of Papers on Radiation Chemistry and Photochemistry*, is produced from the data base and distributed to subscribers. Experimental data for reaction intermediates produced by light or ionizing radiation are compiled from the published literature. Data are included for photochemical and photophysical processes in solution. The data are stored in computer-readable files and are readily available for correlation and reformatting in various ways. Critical reviews of these data are prepared for publication. A goal of this program is the development of a numeric data base of kinetic and spectroscopic properties of reaction intermediates which can be effectively used by many types of users. These bibliographic and numeric data bases are expected to be of increasing importance in the basic scientific study of chemical processes in irradiated systems and in technological applications such as solar energy utilization and photochemical effects on the environment. [2.0 FTE]

**39. Radiation Induced Reactions**

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

A wide variety of chemical reactions induced by the absorption of ionizing radiation are being examined using the Laboratory's broad base of highly developed chemical and instrumental methods for examining intermediates, both in time resolved studies and by analysis of ultimate products. Improvements in dosimetry and time resolution at the LINAC pulse radiolysis facility allow detailed optical and conductometric pulse radiolytic studies to be carried out at nsec and longer times. Recent introduction of laser resonance Raman techniques allows parallel studies of time resolved vibrational spectra of intermediates. Currently, focus is on the molecular and electronic structure of oxygenated radicals present in electron transport processes. Radiation chemical studies are also being carried out at the Notre Dame Heavy Ion Facility to examine track effects in radiation chemical reactions induced by low Z ions having LETs of 1-100 eV/Angstrom. Studies are also being carried out at very high pulse intensities to examine the products of second order reactions between radicals using a Febetron as a radiation source. [21.0 FTE]

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

**Solar Fuels Research Division**

**\$625,000**

**40. Photophysics and Photochemistry of Porphyrins and Model Systems For Artificial Photosynthesis**

*J.S. Connolly*

This project is concerned with fundamental studies of energy- and electron-transfer processes of excited states in a variety of porphyrin-related systems. The focus is on detailed photophysical properties of porphyrins and on light-induced electron transfer in synthetic models of photoreaction centers. The goal is to contribute to an improved understanding of the molecular properties required for efficient light-induced electron transfer in artificial photosynthesis. Laser flash photolysis, fluorescence, and spectroscopic studies are being carried out on covalently linked porphyrin-quinones and on their unlinked constituents to sort out the effects of photophysical properties, redox potentials, molecular geometry, temperature and solvent properties (dielectric constant, viscosity) on the kinetics and mechanisms of light-induced electron transfer and subsequent charge stabilization. [0.8 FTE]

**41. Modified Semiconductor Electrodes For Solar Energy Utilization**

*A.J. Frank*

This research program addresses the fundamental problems of the photoinstability of n-type semiconductors and the high overpotential associated with specific chemical reactions such as the reduction and oxidation of water. Interfacial chemistry, energetics and surface dynamics are established by (photo)electrochemical measurements, end-product analyses, and surface characterization studies. Information obtained from the physicochemical investigations provides guidance for chemically modifying the semiconductor surface to improve photostability and kinetics of desirable redox reactions. The utility of coating the semiconductor surface with electrically conductive polymers in combination with catalytic dispersions

of several transition metals is demonstrated for the visible light-induced water-cleavage reaction. Further development and study of conductive polymers and catalytic surface structures involving coordination metal complexes are in progress. The degree of stability and catalytic activity produced is remarkable and provides encouragement for the potential application of catalytic conductive polymer films to practical photoelectrochemical devices for solar energy conversion. [1.0 FTE]

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

Basic research in photoelectrochemistry is being conducted in the following three areas: (1) hot carrier effects; (2) energetics, kinetics, and characterization studies of semiconductor-electrolyte interfaces; and (3) photoelectrochemical properties of colloidal and particulate semiconductors. Studies of hot electron injection processes from semiconductors into electrolytes are being extended to redox couples lying within the semiconductor band gap. Hot electron reduction of  $H^+$  to  $H_2$  on p-InP is being modeled, and theoretical current-voltage characteristics are being compared to experimental results. The relationship of hot carrier processes to catalytic processes is being analyzed, as well as the theoretical conversion efficiency of Type I hot carrier injection. Computer controlled techniques of photocapacitance, photocurrent and photovoltage spectroscopy, and Mott Schottky analysis are being developed. The techniques of pulse radiolysis and Moessbauer spectroscopy are being used to characterize the photoelectrochemical properties of semiconductor colloids and particles. The flat-band potentials and charge transfer kinetics of several semiconductor colloids and powders have been measured as a function of particle size. Size quantization and hot carrier effects in very small sized (<50 Angstrom) semiconductor colloids are being investigated theoretically and experimentally. [2.8 FTE]

## Chemical Physics

Ames Laboratory  
Ames, Iowa 50011

Division of Fundamental Interactions      \$640,000

#### 43. *Statistical Mechanics of Non-Equilibrium Systems* D.K. Hoffman

Statistical mechanics is used to develop kinetic theory of polyatomic gases in which transport, relaxation, and reactive processes are of interest. Classical and quantum mechanical scattering theory is utilized in the development of collision models to describe energy transfer and reaction between molecules with internal structure. The dynamics and statistics of distributions of molecules adsorbed on surfaces under non-equilibrium 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 includes an investigation of the effect of surface coverage on the nature of binding sites, an exploration of interactions between adsorbed surface species, a study of surface migration and cluster formation, and adsorbate effects on the catalytic properties of surfaces. These models for irreversible lattice processes are also applied to other (non-surface) systems. [1.95 FTE]

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

This project involves crossed molecular beam studies bearing on the kinetics of fundamental processes in combustion and low pressure pyrolysis of hydrocarbons. It also includes the molecular dynamics of excited atoms and molecules, ion/molecule reactions, and high resolution photoionization of molecules, clusters, and transient radicals. A coaxial reactor is being developed for photoionization sampling of reactions involving oxygen atoms and simple hydrocarbons. An important aspect of the work is to understand the role played by stable molecules, intermediate radicals, and ions in flames. [3.43 FTE]

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

Molecular properties, geometric electromagnetic and spectral, and in particular, energy changes during chemical reactions are determined through quantum chemical calculations of molecular electronic structures. Reaction energies and activation energies for elusive intermediates and transition states are predicted. Electronic rearrangements along reaction paths and their energetic and kinetic implications are analyzed. Fundamental developments in many-electron quantum mechanics including electron correlation are made, with the aim of achieving chemical accuracy by practical methods for predictions of reaction mechanisms. Quantitative interpretative concepts are developed for use by non-theorists to analyze reliably and anticipate intuitively *ab initio* predictions. Oxidation-reduction and exchange reactions involving carbon, nitrogen, oxygen, hydrogen, and silicon are studied, in particular reactions occurring in combustion, in the atmosphere, and during hydrogenations. [2.76 FTE]

#### 46. *Ion Chemistry—Mass Spectrometry* H.J. Svec, G.D. Flesch

This research involves the ion chemistry of inorganic, organometallic and organic compounds and ions and complementary neutral fragments produced by electron bombardment. The latter leads directly into the chemistry of highly excited molecules and free radicals. The results bear directly on the origin of aromatic heterocyclic hydrocarbons produced in the combustion of natural gas, oil, wood, and coal under fuel rich conditions. [1.45 FTE]

Argonne National Laboratory  
Argonne, Illinois 60439

Division of Chemistry      \$1,770,000

#### 47. *Theoretical and Computational Chemistry* T.H. Dunning, Jr., R.A. Bair, M.J. Davis, L.B. Harding, R.L. Shepard

This program concentrates on theoretical studies of the energetics and kinetics of chemical reactions, with an emphasis on reactions of importance in the oxidation of hydrogen and simple hydrocarbon fuels. The basic thrust of the project is on calculation of accurate molecular interaction potentials, study of the chemical dynamics on the computed (or other realistic) potential energy surfaces, and characterization of the molecular species (including ephemeral species) involved. In addition, in FY 84 an exploratory program was initiated which will concentrate

on theoretical studies of small clusters of transition metal atoms. The basic thrust of this program will be on the characterization of the electronic structure of the clusters. Finally, there is a continuing effort devoted to development of the theoretical and computational methodology needed to provide a realistic description of these fundamental chemical processes. [7.2 FTE]

**48. High Resolution Spectroscopy and Excited-State Dynamic Processes**

*J.P. Hessler, F.S. Tomkins*

The goal of this program is to elucidate the complex chemical processes needed to describe the behavior of polyatomic molecules which have been excited with vacuum-ultraviolet light. At this relatively high excitation energy the processes of autoionization, predissociation, direct molecular fragmentation, and the decomposition of "superexcited" states are important. High-resolution ( $\delta E/E \approx 10^{-6}$ ) excitation sources are used to selectively excite specific predissociative and Rydberg states of polyatomic systems which have been cooled by the supersonic free-jet expansion technique. A unique feature of this program is the development and utilization of a picosecond laser source which operates in the energy region between 5 and 11.3 eV (250 to 110 nm). With this source the development of the system is followed with 10-picosecond time resolution. The triatomic systems being studied include CO<sub>2</sub>, H<sub>2</sub>O, and XCN (X = H, D, I, Br, and Cl). [2.9 FTE]

**49. 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 (Ni, Cr, V, Ag, Cu, Al, Fe) atom clusters containing 2 to 200 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 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. [5.6 FTE]

**Brookhaven National Laboratory  
Upton, New York 11973**

**Dept. of Applied Sciences \$583,000**

**50. Kinetics and Mechanisms of Alternative Fuels Combustion**

*R.B. Klemm, J.V. Michael, J.W. Sutherland*

The aims 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 alcohols and hydrocarbon synfuels. In pursuing the goals of this project, a facility has been developed that features a variety of experimental techniques including: (1) flash photolysis-resonance fluorescence (FP-RF); (2) discharge flow-resonance fluorescence (DF-RF); (3) flash photolysis-shock tube-atomic absorption (FP-ST-AA); and (4) discharge flow-photoionization mass spectrometry (DF-PIMS). The

FP-RF and DF-RF methods are used in determining specific rates of elementary atom-molecule and radical-molecule reactions over a wide temperature span, ~200-1100K. The recently developed flash photolysis-shock tube apparatus extends the high temperature capabilities for direct rate measurements by a significant extent. With this device, kinetic studies are performed over a temperature range from about 800K to about 2200K; and thus these measurements overlap the temperature range of the other, more conventional techniques utilized in this project. The DF-PIMS method is used in this project in an effort to make direct observations of reactants and products for elementary reactions to investigate the relevant reaction mechanisms. This DF-PIMS experiment utilizes the National Synchrotron Light Source (NSLS). [6.0 FTE]

**Dept. of Chemistry \$2,668,000**

**51. Theoretical Chemistry**

*S. Ehrenson, J.T. Muckerman, M.D. Newton*

The goals of this project are to apply theoretical methods to the study of energy flow in chemical reactions and 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 (i.e., solvation and charge-transfer processes). The methods principally used are *ab initio* and semiempirical calculations of the energies and structures of molecules in specific electronic states, and 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 the data obtained in experimental projects in the Department. [7.1 FTE]

**52. Ion-Molecule Reactions With Applications to Fusion Energy Systems**

*L. Friedman, R.J. Beuhler*

The development of high molecular weight mass spectrometric techniques has provided a facility for the investigation of nucleation processes responsible for the formation of cluster ions and neutral microclusters. Immediate goals are the development of cluster-ion sources and their exploitation as a basic research tool. A high molecular weight mass spectrometer that has the capability of mass analysis of molecular species with *m/e* values up to approximately 200,000 is now in use. Efforts to expand this mass range to higher *m/e* values are pursued, using high voltage ion post-acceleration, and development of time-of-flight mass analytical techniques. Ion source facilities capable of generation of plasmas from gases cooled to temperatures as low as 10 K will be used to study cluster ion generation from inert gases and diatomic molecular species. The generation of cluster ions from hydrogen isotopes is considered a major project objective because of the potential role these cluster-ions may have in the study of controlled thermonuclear reactions. Use of clusters, accelerated to high kinetic energy, to imprint structure on solid surfaces with the generation of microscopic cavities or holes in thin films has been investigated as an additional, technically important application of cluster ion beams. [6.7 FTE]

**53. Gas-Phase Photoionization and Photoelectron Spectroscopy of Molecules and Clusters**

*J.R. Grover, M. White*

Fundamental data necessary to understand fast, exothermic gas phase reactions are being measured via photoionization of molecular beams. This work utilizes tunable, monochromatic radiation from the gas-phase beamline on the VUV storage ring at the NSLS. Excitation function measurements on mass-selected ions are being carried out for van der Waals and hydrogen-bonded dimers and clusters, free radicals, and molecules. From these data, heats of formation and binding energies are determined for both neutral and ionized species, especially neutral dimers, and studies are made of the Rydberg structure and dissociative ionization pathways of molecules and weakly-bound dimers from which an inner-valence electron has been excited or ejected. A general photoelectron spectroscopy study of the ionization dynamics of neutral molecular excited states utilizing both synchrotron and laser radiation is also under way. Photoelectron energy spectra are taken following VUV single-photon excitation or resonant, multiphoton ionization via excited vibronic levels above and below the ionization threshold, respectively. From the observed electronic and vibrational state distribution of the ion, it is possible to investigate in detail the electronic structure and ionization dynamics of electronically excited states of neutral molecules. [4.2 FTE]

**54. *Structure and Bonding of Solids and Molecules On Their Surfaces***  
*J. Hrbek, T.K. Sham*

The main objective of this research program is to improve the understanding of (1) the electronic interactions between surfaces and adsorbates, and (2) the interactions among atoms in condensed matter, with emphasis on 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 help 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, such as photoelectron and x-ray absorption (XANES and EXAFS). The results of these studies are directly related to kinetic and mechanistic aspects of chemical reactivity and catalysis. [3.5 FTE]

**55. *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. Completion of 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 program include organometallic compounds, transition-metal hydrides, zeolites, fast-ion conductors, and dielectric materials. [4.6 FTE]

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

Studies of the structure and reactivity of molecular fragments are important in our understanding of gas phase chemical reaction pathways and rates. Infrared laser techniques are to be applied to the study of these species, which are usually unstable and present only in trace quantities in reaction mixtures. Analysis of the spectra will lead to details of molecular structure, intra- and inter-molecular potential functions, and estimates of the concentrations of reaction intermediates involved in the course of reactions important in combustion and in semiconductor technology. [1.5 FTE]

**Lawrence Berkeley Laboratory**  
**Berkeley, California 94720**

**Applied Science Division**

**\$125,000**

**57. *Unimolecular Kinetics***  
*N. 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 is concerned with the application of theoretical chemical kinetics to study high temperature kinetics important in combustion. Emphasis has been placed upon investigating the dynamics of reactions using classical trajectories. Unimolecular and bimolecular reactions are investigated with realistic potential energy surfaces. Special emphasis has been placed upon 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. A second activity is concerned with investigating the ignition chemistry of hydrocarbon/air mixtures. Identification of the principal elementary reaction steps which occur during ignition of hydrocarbon/air mixtures and determination of the corresponding rate coefficients are required to achieve an understanding of ignition. Initially, ignition will be investigated in a static system and the time-resolved evolution and decay of active radical species will be monitored. Temporal measurements of radical concentrations will be achieved with a molecular beam mass spectrometer and with spectroscopy. [1.25 FTE]

**Materials and Molecular Research**  
**Division**

**\$2,326,000**

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

A proper description of the ways in which internal energy is transferred between molecules and surfaces through electromagnetic field interactions, particularly in the short distance regime, is crucial to the understanding of a wide variety of molecule-surface interactions including laser induced photoionization and photochemistry at metal and semiconductor surfaces. In addition, surface enhanced electromagnetic field interactions are fundamental to other phenomena such as surface Raman scattering and other non-linear interactions. The long-range goals of this research are (1) to study and understand the general principles that underlie electronic and vibrational energy redistribution at metal surfaces, and (2) to develop new laser techniques for characterizing metal surfaces and chemisorbed

molecules in the visible and vibrational infrared portion of the electromagnetic spectrum. [2.2 FTE]

### 59. *Crossed Molecular Beams*

*Y.T. Lee*

The major thrust of this research project is to elucidate detailed dynamics of simple elementary reactions which are theoretically important and to use the molecular beams method to unravel the mechanisms of complex chemical reactions or photochemical processes which 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 direct probing of transition states of the  $F + H_2$  reaction through the experimental observation of quantum mechanical resonance phenomena, the mechanisms of elementary chemical reactions involving oxygen atoms with unsaturated hydrocarbons, the dynamics of chemical reactions of electrochemically excited atoms, the primary photochemical processes of polyatomic molecules radicals and ions, intramolecular energy transfer of chemically activated and locally excited molecules using overtone excitation processes, and the interaction potential of open shell atoms with rare gas atoms. [8.0 FTE]

### 60. *Molecular Interactions*

*W.A. Lester, Jr.*

This program is directed at extending fundamental knowledge of the interactions that govern the dynamics of energy transfer, reactive, and photodissociative molecular processes. The approach is based on the reliable description of the potential energy surfaces and coupling matrix elements needed in theoretical approaches for the evaluation of cross sections and rates. Emphasis is placed on the use of state-of-the-art Hartree-Fock (HF), multiconfiguration HF, and configuration interaction (CI) *ab initio* methods for the accurate description of molecular interactions. A variety of methods are used to describe collision dynamics. The electronic structure studies emphasize the determination of the critical geometries and energetics that govern reaction pathways and include the computation of global potential energy surfaces where appropriate. The dynamics studies include fully quantum mechanical approaches to ro-vibrational energy transfer in molecules by collision, and an adiabatic approach to single-photon photodissociation of small polyatomic molecules and to chemical reaction. A novel method that solves the Schroedinger equation stochastically is also being studied to ascertain its usefulness for determining the energy and other molecular properties. [3.5 FTE]

### 61. *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 one to combine 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 carrying out 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. [3.8 FTE]

### 62. *Selective Photochemistry*

*C.B. Moore*

The goals of this program are to understand the photophysics of selective excitation of molecules, dynamics of energy transfer and specificity loss, and the chemical reactions of specifically excited states. Low levels of vibrational excitation in small molecules, chemical reaction rate constants are defined for each quantum state. Larger, more highly excited molecules, energy is usually transferred among vibrational modes more rapidly than chemical reactions occur. 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 possibilities for limitations upon selectivity in photochemical processes are determined by the time evolution of the combination of spectroscopic states excited by the photons. A complete understanding of unimolecular dynamics is sought by both the examination of spectra and the measurement of reaction rates. Rates and mechanisms of free radical reactions are often best studied by flash kinetic spectroscopy using laser, for thermal heating, for photolyzing, and for spectroscopic probing. A fundamental understanding of these reactions is ought to serve as a basis for modeling combustion processes. Radical-radical collisions can lead to complex formation. Consequently, reactions and energy transfers between radicals can be understood in terms of unimolecular reactions. [3.0 FTE]

### 63. *Physical Chemistry With Emphasis On Thermodynamic Properties*

*K.S. Pitzer*

The purpose of this program 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. Recent theoretical advances include treatments of the dielectric constant of  $H_2O$ , the thermodynamics of ionic solutions in  $H_2O$  above its critical temperature, and the critical properties of pure ionic fluids such as  $NaCl$ . Earlier advances yielded improved equations for electrolyte solutions which are now being applied to a wide variety of systems of industrial or geological interest including geothermal brines. Current efforts also include relativistic quantum mechanical methods for the calculation of energies, bond dis-

tances, 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 evaluation of possible laser systems and for models of catalytic entities including heavy atoms such as platinum. [2.2 FTE]

#### 64. *Spectroscopy and Structures of Reactive Intermediates*

*R.J. Saykally*

The principal objective of this program is to study spectra, structures, and properties of elusive reaction intermediates that are of importance in combustion processes. Present emphasis is on the development of three powerful new spectroscopic techniques for detecting very low concentrations of such reactive intermediates. A far-infrared laser magnetic resonance (LMR) spectrometer employing selective UV photolytic generation of the reactive species is presently being tested; optimization of the experimental parameters for study of the hydroxyl radical has been accomplished. Extension of this approach for the study of important carbene species (HCOH, HCCN, CH<sub>2</sub>) is in progress. A totally new laser spectroscopy experiment has been developed. Molecular Beam Laser Electronic Resonance (MBLER), in which ultra cold (10-50°K) reactive molecules are generated in supersonic beam inside the cavity of a far-infrared laser and rotational transitions are tuned into resonance with the laser with a large DC electric field, compliments the capabilities of Laser Magnetic Resonance for the study of reaction intermediates. The system is being tested on stable molecules (CH<sub>3</sub>F, PH<sub>3</sub>) and will be extended to prototype reactive intermediates (OH, CH, CH<sub>2</sub>) in the near future. The first measurement of the dipole moment of methylene (CH<sub>2</sub>) is anticipated. [3.7 FTE]

#### 65. *Potential Energy Surfaces For Chemical Reactions*

*H.F. Schaefer, III*

This research program has two goals, related yet distinct. The first goal is the development of new theoretical and/or computational methods for the description of "what electrons are doing in molecules," to use the words of Robert S. Mulliken. Specifically, 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 of research is to apply these theoretical methods to significant problems of broad chemical interest. Currently, two areas are of special interest: (1) model theoretical studies of chemisorption, metal clusters, and organometallic species; and (2) potential energy surfaces which 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. It is to be emphasized that in recent years theoretical chemistry has become a significant source not only of broad generalities, but also of specific predictions concerning molecular systems which may be very important but inaccessible to experiment. [5.5 FTE]

#### 66. *Photoelectron Spectroscopy*

*D.A. Shirley*

This program addresses experimental aspects of electron spectroscopy to investigate the electronic structure of matter. General areas under study include: (1) electron spectroscopy, electronic structure of matter, as determined by photoelectron spectroscopy and related techniques; (2) the electronic structure of gas-phase species, including high-temperature species, as determined by the use of pulsed synchrotron radiation, including absorption and time-of-flight photoelectron spectroscopy; (3) photoelectron angular distributions and correlation-state studies; (4) electronic structure of solids from angle-resolved, variable-energy photoemission; (5) atomic and electronic structure of surface-adsorbate systems; (6) photoelectron spectroscopy of metal clusters and other exotic species; and (7) exploration and development of new experimental methods based on synchrotron radiation in the energy range 10-4000 eV, such as photoelectron diffraction, ARPEFS, and surface EXAFS. [10.5 FTE]

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

Chemistry Division

\$438,000

#### 67. *Molecular Research With Electron Spectroscopy*

*T.A. Carlson, M.O. Krause*

A basic study of the photoelectron dynamics of molecules and metal vapors is being undertaken through the use of angle-resolved photoelectron spectroscopy and synchrotron radiation. Phenomena receiving particular attention include: (1) the Cooper minimum; (2) shape resonances; (3) autoionization; (4) correlation satellites; and (5) interchannel coupling. Systematic studies are being pursued on halogen acids, freons, nitrous oxide, and various metal vapors including Ag, Ga, Pb, and some 3d transition metal elements. Supportive calculations using the multiple scattering X Alpha method are being performed and correlated with observed cross sections and angular distribution parameters. Improved computer handling of the experiment has allowed the introduction of constant-ionic-state techniques. Besides providing fundamental information in atomic and molecular science, the program supplies data and ideas for studying molecules adsorbed on surfaces, clarification for solid state properties in metals, and an understanding of clusters. [2.6 FTE]

#### 68. *Photochemical, Pyrolytic, and Reactive Intermediates By Electron Spin Resonance*

*R. Livingston*

Labile free radicals are observed at steady state concentration by ESR in circulating fluids at pressures up to 200 atm and temperatures to 700°C. Radicals are formed pyrolytically and photolytically with and without the use of added radical initiators such as peroxides. Work has centered largely on substances that are constituents of fuels and that are related to the production and combustion of organic fuels. Chemical product assays give additional information that is correlated with the kinetic parameters. Specific studies include properties of allyl radical and thermolysis of dibenzylamine. [0.3 FTE]

**Sandia National Laboratories**  
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**Combustion Sciences Dept. \$5,260,000**

**69. 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 in this work are the dynamics of carbonaceous particulates in sooting flames and the ignition, free propagation, and quenching of transient gas-phase flames. An important aspect of this work 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 time-dependent interaction of a laminar flame with a single vortex, and the generation and evolution of the OH molecule during the interaction. Comparison of these results with the modeling predictions generated using the vortex dynamics computational method have been made. Soot size and number density, and the effect of increasing pressure on these quantities, have been determined in a laminar diffusion flame. Species thought to be responsible for soot particle surface growth have been detected using coherent anti-Stokes Raman spectroscopy. [3.0 FTE]

**70. 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. Multi-species Raman concentration and temperature measurements, combined with simultaneous velocity determinations, have been compared with model predictions to estimate the influence of chemical non-equilibrium on mean turbulent flame quantities. A new laboratory incorporating a vertical flame tunnel (and making use of the CRF facility dye laser) is fully operational. A chemically reacting turbulent flow cooperative group comprised of participants from private industry, universities, and Sandia has been formed and meets on a regular basis. [3.0 FTE]

**71. Combustion Research Facility Operations and Visiting Scientist Support**  
*G. Drummond, D. Benthussen, R. Johnsen*

This task supports all phases of Combustion Research Facility operations: (1) operation of the central Facility lasers; (2) operation and maintenance of the Facility VAX computer and networked minicomputers; (3) operation of the computer terminals to the Sandia CRAY; (4) staffing of the shop and analytical laboratories; and (5) maintenance of the safety and control system. This task also provides support for visiting scientists and for the transfer of technology developed and implemented at the Facility to others in the combustion community. Visitor support includes technician, scientific, engineering, and administrative staff dedicated to the visitors' project, as well as computer time, shop work, and purchases used directly by visitors or in support of them. The transfer of technology activity provides technical information to industry and university scientists through short courses in specialized areas, workshops on relevant topics, and combustion-related meetings and seminars. [13.0 FTE]

**72. CRF Diagnostics Research: Coherent Raman Processes**

*R. Farrow, L. Rahn, R. Lucht, R. Palmer*

This research effort is directed toward developing coherent Raman diagnostic techniques in support of Combustion Research Facility programs. New normalization techniques are being refined for coherent anti-Stokes Raman spectroscopy (CARS), a leading technique for time-resolved measurements of major species concentrations and temperatures. These new *in situ* normalization schemes provide accurate corrections to fluctuating CARS signals in high-pressure environments, and have been implemented in a CRF internal combustion engine experiment. The effects of Stark broadening and laser photon statistics on absolute concentration measurements are being explored. High-resolution inverse Raman spectroscopic measurements are providing precise high-temperature N<sub>2</sub> and CO lineshape data. The vibrational Stark effect discovered earlier is being quantified in a crossed-beam infrared absorption experiment to provide spatially precise CO spectra from a laboratory flame. [3.0 FTE]

**73. CRF Diagnostics Research: Advanced Methods**

*J. Goldsmith, M. Koszykowski, F. Tully, R. Palmer*

This project supports three broad areas of diagnostic research: (1) development of new multiphoton nonlinear techniques for detecting trace species in combustion environments; (2) research on advanced methods for kinetics studies; and (3) theoretical studies in support of CRF projects. In the first area, atomic hydrogen has been observed in a flame using multiphoton opticalgalvanic spectroscopy, representing the first direct *in situ* optical detection of this important radical in a combustion environment. Atomic oxygen and NO have also been studied with this technique. These methods are being used to map out H and O atom relative profiles in flat flames, and the capabilities and limitations for making absolute concentration measurements are being determined. Spatially resolved absorption methods are being developed for measuring other radicals in flames. Kinetics studies based on pulsed-laser photolysis followed by ultraviolet laser induced fluorescence have been extended to higher sensitivity by using a cw intracavity-doubled ring dye laser. Theoretical techniques involving electronic structure and scattering calculations, as well as approximate chemical kinetic theories, are being applied to a variety of CRF projects, including high-resolution spectroscopy, lineshape modeling, and kinetics studies. [3.0 FTE]

**74. Flame Chemistry: Modeling and Experiments**

*W.J. McLean, J.A. Miller, M.D. Smooke, L.R. Thorne, R.W. Schmieder*

The principal objective of this research is the development of comprehensive models for the chemical processes which govern flames. Emphasis is placed upon 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.

During the past year, combined modeling and experimental studies were used to produce a comprehensive model for the conversion of HCN to N<sub>2</sub> and NO in flames. A detailed model for the structure and extinction limit of a methane-air counterflow diffusion flame was developed, and compared with experimental data. Experiments and computations are in progress to examine the chemical structure of premixed flames containing nitrogen and sulfur contaminants. Diffusion flame experiments using hydrocarbons labeled with carbon-14 at specific sites are being carried out to determine the propensity for particular molecular fragments to be incorporated into flame generated soot. [4.0 FTE]

**75. Chemical Kinetics and Dynamics**  
*W.J. McLean, F.P. Tully, R.A. Perry, D.W. Chandler, C. Melius*

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 chemiluminescence and 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 also 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 intra-molecular energy transfer on unimolecular reactions is studied using dynamical methods. [4.0 FTE]

**76. CRF Central Laser Systems**  
*R. Schmitt, R. Farrow, R. 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 operational, with performance levels which meet or exceed design specifications in all significant characteristics. Beam delivery and control throughout the Facility have been implemented. SNLL and visiting scientist experiments are now routinely using Diana. Possible system improvements include frequency doubling to obtain radiation from 240 to 370 nm, and mode-locking to obtain subnanosecond pulses. A new multipurpose laser system, Sirius, has been installed and used for CARS measurements in several different experiments. This new facility laser system, when fully completed, will provide several sources of high peak power, ultra-high resolution radiation, thereby adding CARS and other nonlinear spectroscopic capabilities to all of the CRF laboratories. A third central laser consisting of a frequency-doubled pulsed Nd:YAG laser is being installed to provide additional capability to pump dye lasers in remote user laboratories. [3.0 FTE]

## Atomic Physics

### Argonne National Laboratory Argonne, Illinois 60439

Division of Physics \$1,930,000

**77. 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, providing 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 UV-laser radiation with selected molecular ions. [3.9 FTE]

**78. Atomic Spectroscopy With Fast Beams At ANL**  
*H.G. Berry, L. Young*

Measurements of 2s<sup>3</sup>P<sub>1</sub>-2p<sup>3</sup>P<sub>0,2</sub> transition wavelengths in highly-stripped two-electron atoms are continuing at the Argonne Tandem-Linac with ions of titanium. A new linear position-sensitive detector is being developed to replace the grating exit slits. A program of experiments utilizing laser excitation of fast ion beams has begun. Several experiments involving ion beam resonant excitation by collinear laser beams are under construction. Our first observations have been made of single photon and doppler-free two photon excitation in neon. An immediate goal is improvement of the accelerator voltage stability from 100 volts at present to less than 5 volts. Further measurements in hydrogen, helium, lithium, and sodium are in progress. Optical polarization measurements have been made of the light emitted from excited states of hydrogen and hydrogen-like helium following perpendicular and tilted carbon-foil excitation of protons, H<sub>2</sub><sup>+</sup> and He<sup>+</sup>, at energies of 50-100 keV and 0.7 to 1.7 MeV. Strong alignment and orientation for highly excited states have been observed. They indicate a strong projectile-produced surface electric field of up to several mm in spatial extent. Beam-foil spectroscopy of multiply-excited states in light ions is continuing. We are also studying the fluorescence of atomic fragments of molecular ions following carbon foil break-up at Dynamitron energies. [4.4 FTE]

**79. Theoretical Atomic Physics**  
*K.T. Cheng*

This program is directed toward a detailed understanding of the role of relativity and electron correlation in atomic processes. The emphasis is on photoexcitation and photoionization where one can gain important insight into the dynamics of many-electron interaction in atoms and ions. Current efforts include the systematic study of the ground-state hyperfine structures of rare-earth elements using a technique based on the multiconfiguration Dirac-Fock method. The same technique is used to study the fine and hyperfine structures of the Li<sup>+</sup> ion which are very sensitive to Breit interaction and electron correlation effects. Studies are also being carried out on the changes in the

correlation effect along an isoelectronic sequence as reflected in the profiles of the autoionization resonances. The purpose of this study is to gain better understanding of the dynamics of Rydberg series interactions. [1.1 FTE]

**80. High-Resolution Laser-rf Spectroscopy With Atomic and Molecular Beams**  
*W.J. Childs, L.S. Goodman*

This program is directed toward a detailed understanding of interactions in 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. Within the last year the experimental methods have been extended to make possible measurement of the electric-dipole moments of such radicals. A similar program aimed at a systematic understanding of the hyperfine interaction throughout the 4f-shell of the rare-earth atoms is under way concurrently. A new apparatus for analogous studies of atomic and molecular ions using collinear laser and radiofrequency spectroscopy is under development. [3.1 FTE]

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

Argonne's 4.5-MV Dynamitron accelerator is used to study the interactions of fast (MeV) atomic and molecular ions with matter. A unique feature of the apparatus is the exceptionally high resolution (0.005° and 300 eV) in angle and energy obtained in detecting particles emerging from the target. The apparatus also permits the coincident detection of up to three molecular dissociation fragments. The work has as its main objective a general study of the interactions of fast charged particles with matter, with emphasis on those aspects that take advantage of the unique features inherent in employing molecular-ion beams (e.g., the feature that each incident molecular ion forms a tight cluster of atomic ions that remain correlated in space and time as they penetrate the target). In addition, we are able to study the structures of the molecular ions that constitute the incident beams. Current attention is being focused on the production of highly-excited Rydberg atoms formed in foil-excited ion beams. [4.9 FTE]

**Brookhaven National Laboratory**  
Upton, New York 11973

Dept. of Physics \$255,000

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

Beams from the Brookhaven Double Tandem Van de Graaff Facility are used to study various aspects of ion-atom and ion-electron collisions. Energies for negative ions cover the range from about 1 to 9 MeV. Beams of almost fully stripped elements up to iron can be produced with energies from several MeV to several hundred MeV when the tandems are operated in the accel-decel and three-stage configurations. A lesser degree of ionization is obtained for heavier elements. 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. Inner-shell vacancy processes are also studied with these beams. An effort to measure electron ionization

and excitation cross sections in an electron-heavy ion crossed-beam experiment is now in progress. Work to study the excitation and ionization of atoms and ions by photons from the National Synchrotron Light Source has been started. Design and fabrication of the beam line has commenced with first operation anticipated in 1984. Experimental apparatus for the initial experiments is currently being assembled. [3.1 FTE]

**Lawrence Berkeley Laboratory**  
Berkeley, California 94720

Materials and Molecular Research \$410,000  
Division

**83. Atomic Physics**  
*R. Marrus*

This program is concerned with a broad-ranging experimental study of collisions and spectroscopy in simple atomic systems. Particular emphasis is placed on those processes pertinent to controlled thermonuclear reaction devices and processes important to fundamental physical laws. Examples of such studies are: (1) electron capture by low-energy multicharged ions; (2) x-ray spectroscopy of heliumlike, lithiumlike, and berylliumlike ions of high Z; (3) parity violation in heavy atoms predicted by unified theories of weak and electromagnetic interactions; (4) charge capture and loss by fast multicharged atoms in solid and gas targets; and (5) study of quantum electrodynamic effects and relativistic effects in hydrogenic and heliumlike uranium. These studies take advantage of unique facilities developed within the group or available at LBL. Examples of such facilities are: (1) LBL's SuperHILAC and Bevalac that produce a range of heavy ion beams at energies greater than any other facility in the world; (2) ion trapping techniques developed within the group (making possible the application of this technique to more highly ionized states than have heretofore been achieved); and (3) narrow band, high-power UV lasers developed within the group for studying parity violation in atomic systems. [6.0 FTE]

**Oak Ridge National Laboratory**  
Oak Ridge, Tennessee 37831

Physics Division \$1,240,000

**84. Theoretical Atomic Physics**  
*R.L. Becker, C. Botcher*

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 ORNL Holifield heavy ion accelerator), subshell vacancy production including the effects of vacancy rearrangement processes, electron capture and ionization in the nearly symmetric system  $F^{9+} + Ne$  at both low and high impact speeds, 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 finite elements 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 in the last year. [1.0 FTE]

#### 85. *Accelerator Atomic Physics*

*S. Datz, P.F. Dittner, P.D. Miller, C.D. Moak*

The objective of this task is to achieve a detailed understanding of the interactions of high-energy, multiply charged, heavy ions with gas, solid, and electron targets. The primary facility used is the EN-tandem accelerator. Ion-ion collisions at low energies are also being investigated, and two experimental programs have been started on the Holifield accelerators. Examples of subjects which have received particular attention during the past year are: (1) cross section measurements of dielectronic recombination of  $O^{5+}$  and  $Cl^{6+}$  using a merged multiply charged ion beam concentric with an electron beam; (2) dependence of dielectronic recombination on stripping fields for  $C^{3+}$ ; (3) transverse correlation effects on ion channeling trajectories; (4) production of polarized highly stripped ions by electron capture in ferromagnetic crystal channels; (5) mechanisms for transfer ionization; (6) continuing study of positron and electron channeling radiation; and (7) charge changing ion-ion collisions. Results in these areas impinge directly on fusion research, solar corona studies, and material sciences, as well as improving fundamental understanding of ion-atom, ion-solid, ion-ion, and ion-electron interactions. [5.9 FTE]

#### 86. *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 from  $Z=1$  through 9, and many heavier ions are available for users. The user group includes members of the physics division, other divisions of ORNL, faculty and students from various universities, and representatives from industry. During 1983, the installation of the Elbek spectrometer was completed. Calibration is now being done, and the first experiments will be undertaken during 1984. A new data acquisition system is being specified, and will be purchased and installed during 1984 and 1985. The major beam usage during 1983 was for the merged electron heavy ion beams experiments, convoy electron studies, trapping of low energy highly charged ions, and channeling experiments. Approximately 40% of the available beam time was utilized by university users. [1.6 FTE]

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

*R.A. Phaneuf, H.F. Krause*

This experimental program is aimed at improving our understanding of inelastic collision processes involving multiply charged ions at the lowest attainable collision energies. The 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. A pulsed-laser-produced plasma is utilized as a unique source of low-energy, highly stripped ions which are directed through a calibrated

thermal-dissociation atomic hydrogen gas target. Charge and energy analysis is effected by a time-of-flight technique. Total electron-capture cross sections have been measured recently for  $B^{+q}$  ions ( $2 \leq q \leq 5$ ) at energies in the range 10-100 eV/amu, and provide data for testing predicted ionic charge scalings at low energies. An ion-atom merged-beams apparatus is also in final stages of development and testing. This will permit study of such collisions at center-of-mass energies as low as 1 eV/amu, where theoretical predictions of increasing cross sections with decreasing energy remain untested. [1.4 FTE]

### Sandia National Laboratories Albuquerque, New Mexico 87185

Dept. of Laser R & D

\$155,000

#### 88. *Atomic Processes*

*A. Owyong, J.P. Hohimer, A.V. Smith*

This research is directed toward the study of high-order nonlinear optical interactions in atomic and molecular systems, with the goal of uncovering an efficient method for the generation of fully tunable coherent vacuum ultraviolet (VUV) radiation. Present investigations are concentrating on fifth-order, two-frequency summing processes in atomic vapors whereby third harmonic generation at one frequency is enhanced by a second laser source, which effectively couples the process into a four photon resonance with the atomic system. Our investigations will continue to explore phenomena involving such "optically induced structure" in the continuum between states, but will also be extended out to the ionization continuum. These subsequent studies will both extend the accessible VUV tuning range and provide for the exploration of more complex interactions that are expected to occur when resonant ionization becomes a significant consideration. This research project will not only provide a new and potentially very useful means for VUV generation, but also contribute significantly to our understanding of the complex interactions of optical radiation with atomic and molecular systems. [1.5 FTE]

### Chemical Energy

Ames Laboratory  
Ames, Iowa 50011

Processes and Techniques

\$1,006,000

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

*R.J. Angelici*

The major thrust of this research is to understand the role of organometallic complexes in transition metal-catalyzed reactions and to seek new catalytic reactions that provide energy-efficient routes to useful chemicals. Of particular interest are reactions of ethylene oxide with CO. It has been demonstrated that CO ligands in complexes of Fe, Ru, Mn, and Re react with ethylene oxide to form dioxo-carbene complexes of those metals. This type of reaction is being examined for possible catalytic applications. In another area, possible mechanisms for the hydrodesulfurization (HDS) of thiophene are being investigated by

studying the reactivity of  $\pi$ -bonded thiophene in transition metal complexes. Early results indicate that the coordinated thiophene is highly activated to react with transition metal hydrides, a possible reaction occurring on heterogeneous HDS catalysts. [2.7 FTE]

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

Organometallic complexes such as  $(H_2O)_5Cr-R^{2+}$ ,  $R-Co(dmgh)_2L$ , and  $R-Rh(dmgh)_2L$  are under active investigation, as are dinuclear compounds having a metal-metal bond. The research concerns the reactions which occur and their kinetics and mechanisms, especially reactions in which the metal-carbon bond is formed or broken, or in which the organic group, R, reacts further. Novel displacements by free radicals are being investigated using techniques such as stopped-flow kinetics, product competition ratios, stereochemical labeling, and flash photolysis. Included are classes of compounds important in Fischer-Tropsch reactions, such as  $\alpha$ -hydroxyalkyls. Studies of metal-carbon bond homolysis permit: (1) evaluation of thermodynamic bond dissociation energies; (2) resolution of the mechanism of homolytic cleavage vs. competing heterolysis; (3) examination of novel free radical displacement reactions; and (4) evaluation of the kinetic reactivity of aliphatic radicals. Conditions have been developed for the use of metal complexes to generate aliphatic radicals in solution in a controlled manner. Mechanistic studies are also in progress to learn how insertions into metal-metal bonds to form molecular A-frames occur, and to study the reactivity of such compounds. [4.9 FTE]

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

Solid state NMR is used to infer chemical functionality in coals and products of coal conversion (e.g., solid asphaltenes) and to probe hydrogen, silicon, and aluminum in zeolites used for converting methanol to ethylene. In addition, the morphology of proton containing regions in amorphous silicon-hydrogen alloys, and the types of  $SiH_x$  groups present in these materials are studied by solid state proton and silicon NMR using a variety of experiments involving the proton and silicon spin dynamics. [4.0 FTE]

**92. 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 for producing synthetic fuels or for hydrotreating coal-derived liquids are being investigated; catalysts for energy-efficient routes to chemicals are also important in this research. Spectroscopic techniques such as laser Raman spectroscopy and Fourier transform infrared spectroscopy are being used to characterize catalysts and adsorbed species. *In situ* experiments are being performed involving functioning catalysts; simultaneous spectroscopic and kinetic measurements can be performed at temperatures and pressures typical of industrial operating conditions. These techniques provide a direct method for relating structure and composition to cata-

lytic activity, selectivity, and stability. The effects of defect structures, oxidation state, and nonstoichiometry are particularly important for the metal oxide and sulfide catalysts being examined. Adsorption and reaction studies are being performed using pulsed and steady-state fixed bed reactors. [1.9 FTE]

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

This research is directed toward an understanding of the fundamental thermal reactions of organic compounds, especially those that could be important in the pyrolysis of coal and coal-derived liquids. The work can be divided into three main categories: (1) determining the major pyrolysis reactions of model compounds; (2) preparing and studying physical and chemical properties of reactive compounds thought to be intermediates in pyrolysis reactions; and (3) determining the importance of surface-catalyzed reactions under various pyrolysis conditions. Most pyrolyses are carried out using the flash vacuum pyrolysis technique. Much of the work concentrates on the study of pyrolysis reactions that are thought to involve quinodimethanes as intermediates, on preparing and characterizing these and related species, and on thermal reactions of these species and products derived from them. Specific compounds under study include tetralins, 2,3-dimethylene-2,3-dihydrofurans, the furan and thiophene analogs of *ortho*-quinodimethanes, and benzocyclobutenes, and the closed forms of *ortho*-quinodimethanes. [2.2 FTE]

**94. Study of Solid-Gas Reactions Which Involve Structural Changes In the Solid**  
*D.L. Ulrichson, A.H. Pulsifier*

The objective of this project is to understand and describe the behavior of the class of solid-gas reactions which exhibit either expansion or contraction of the solid during reaction. In the case of solid expansion, the increased volume of the solid product closes diffusion paths for the gaseous reactant and stops the reaction at less than total conversion. The reaction of sulfur dioxide with calcium oxide (used to remove sulfur dioxide from boiler flue gas) is an example in which only about thirty percent of the calcium oxide reacts before the reaction stops. Previous models concentrated on the effect of the reduced porosity resulting from product expansion. Data from this project indicate that diffusion of reactant through the solid product layer is as important as pore reduction. Inconsistencies in published results for several solid-gas reactions can be explained by including this term. Current work emphasizes measurement of diffusion rates through the pores and through the solid product layer. [0.5 FTE]

**Argonne National Laboratory**  
 Argonne, Illinois 60439

Division of Chemical Technology

\$468,000

**95. Fluid Catalysis**  
*J.W. Rathke, M.J. Chen, R.J. Klingler, J.J. Heiberger*

This research attempts to determine reaction mechanisms and to develop new catalytic chemistry for converting small molecules (e.g., CO and  $CO_2$ ) to specific desired products. Currently under investigation are the roles of formate and carbonate ions

in the mechanism of operation of a new series of catalysts for reacting carbon monoxide with water or hydrogen to produce alcohols. The new chemistry is unusually general in that it applies to both main group and transition metal centers. Related to this study is an investigation of the precise chemical transformations involved in the activation of hydrogen, carbon monoxide, and carbon dioxide by homogeneous and heterogeneous metal oxide complexes. Also studied is the role of alkali metal promoters in converting methanol to higher alcohols in catalytic alcohol syntheses. The mechanisms of these reactions are being investigated using a combination of high-pressure kinetic, spectroscopic, and theoretical (molecular orbital) methods. [5.3 FTE]

**Division of Chemistry** **\$1,715,000**

**96. Inorganic Fluorine Chemistry**  
*E.H. Appelman, L.J. Basile, L. Stein*

This program has as its objective the synthesis and characterization of novel inorganic oxidants and fluorinating agents, as well as the development of applications of these exotic compounds to other areas of chemistry. Ongoing work includes thermodynamic characterization of  $\text{SO}_4\text{F}^-$  and  $\text{HSO}_5^-$ , evaluation of the acidities of strong acids in anhydrous HF, the use of noble gas compounds to aid the characterization of low-temperature matrices by EXAFS spectroscopy, exploration of the interaction of  $\text{F}_2$  with aqueous solutions, the application of  $\text{SO}_4\text{F}^-$  as a fluorinating reagent for organic and organometallic chemistry, and the study of hydrolytic reactions of radon compounds. [2.4 FTE]

**97. 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 to be as chemically and physically identical as possible, have well-characterized chemical and physical properties, and be stable over long periods of time. Coals are to be mined, transported, processed into desired particle and sample sizes, and packaged in environments which are as free of oxygen as possible and which maintain the natural moisture content to insure that the coals are kept in as pristine and stable condition as possible. These premium samples are to be distributed to researchers upon request. It is anticipated 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. [3.6 FTE]

**98. Fundamental Chemistry of Coals and Other Fossil Fuels**  
*R.E. Winans, R. Hayatsu, R.E. Botto, R.G. Scott, R.M. McBeth*

As its major objective this program seeks to provide a fundamental understanding of the organic structures in coal and coal macerals and to be able to relate this information to the reactivity of these materials. Synthetic coal macerals are being prepared in a unique process. This study provides insight into how macerals are formed and yields well-characterized macromolecular models for coals. Selective chemical reactions, pyrolysis

MS and solids NMR are used for characterization of both synthetic and natural macerals. New separations and identification techniques for large and nonvolatile molecules are being developed for this program. [7.2 FTE]

**Brookhaven National Laboratory**  
**Upton, New York 11973**

**Dept. of Applied Sciences** **\$588,000**

**99. 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. [2.2 FTE]

**100. Metal Hydrides**  
*J.J. Reilly*

The overall concern of this program is the determination of the thermodynamic properties and structural parameters of metal alloy-hydrogen systems. Particular goals are to relate hydriding properties of metal alloys to their structure and composition, determine alloy-hydrogen phase diagrams, determine and systematize crystal structure and, finally, relate all pertinent data and observations for a predictive capability of 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, the partial molar volume of hydrogen in intermetallic compounds, the influence of defects upon system behavior, and reaction kinetics of metal hydride suspensions. The major experimental tools and/or techniques consist of x-ray and neutron diffraction, equilibrium pressure temperature composition measurements, ion beam analysis, and magnetic susceptibility measurements. [4.1 FTE]

**Dept. of Chemistry** **\$416,000**

**101. Organometallics in Homogeneous Catalysis**  
*M.A. Andrews*

The major emphasis of this project is the development of a better understanding of the role that soluble transition metal complexes can have in the homogeneous catalytic oxidation of organic substances. A potential long term benefit of this work includes the discovery of more efficient alkene epoxidation catalysts. The approach currently under investigation takes advantage of the fact that transition metal nitrosyl complexes can symmetrically cleave atmospheric dioxygen to give metal nitro

complexes. These species can then transfer an oxygen atom from the nitro group to an alkene substrate to give epoxides and other oxidized products. The mechanism of alkene oxidation by  $\text{Pd}(\text{CH}_3\text{CN})_2\text{ClNO}_2$  has been studied in detail, primarily through the isolation and characterization of intermediates (alkene and heterometallacyclopentane complexes) and the analysis of product distributions as a function of the alkene substituents and stereochemistry. Future studies will be devoted to the investigation of other metal nitro catalyst systems, the development of oxygen atom carriers besides nitro groups, and more detailed studies of the factors governing the selectivities of these systems for epoxides vs ketones and other beta-hydrogen elimination derived products. [4.2 FTE]

**102. 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 nonthermodynamic mixture of isomers (achieved by irradiation) to the thermodynamic mixture can result in the release of thermal or electrical energy. This cis-trans energy-producing effect is utilized 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 BNL 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. [1.5 FTE]

**DOE/Pittsburgh Energy Technology Center**  
**Pittsburgh, Pennsylvania 15236**

**Analytical Chemistry Branch** **\$93,000**

**103. Vibrational Spectroscopic Studies of Coal Conversion Catalysts**  
*J.M. Stencel*

Research during the current year has concentrated on understanding molybdenum-support and tungsten-support interactions in  $\text{Mo}/\text{Al}_2\text{O}_3$ ,  $\text{W}/\text{Al}_2\text{O}_3$ ,  $\text{Ni-Mo}/\text{Al}_2\text{O}_3$ , and  $\text{Ni-W}/\text{Al}_2\text{O}_3$  catalysts. Raman spectroscopy is the primary tool used to define molecular speciation for catalysts in which Mo, W, and Ni concentrations have been varied systematically. Additional information concerning the influence of concentration and symmetry of the metal oxides on their vibrational frequencies is obtained by *in situ* experimentation and by adsorption of ligand-forming and hydrogen-bonding molecules. Raman experimentation is supplemented by data from other bulk and surface sensitive techniques such as x-ray diffraction, x-ray photoelectron spectroscopy, and ion scattering spectroscopy. Correlations are made with catalytic reaction data to provide insight into structural and chemical factors that influence catalytic activity. [1.0 FTE]

**Lawrence Berkeley Laboratory**  
**Berkeley, California 94720**

**Applied Science Division**

**\$32,000**

**104. Bioconversion of Cellulose**  
*C.R. Wilke, H.W. Blanch*

This project investigates primarily the enzymatic hydrolysis of biomass to hexose and pentose sugars. Basic information on the kinetics and mechanism of enzymatic hydrolysis is to be obtained. This information can then be used to develop low-cost processing schemes for sugar production. High productivity fermentations to convert these sugars to ethanol or other chemical feedstocks are being developed. Fundamental studies on yeast metabolism in high cell density cultures will be obtained. This will be combined with basic studies on ethanol separation from the fermentation broth, using novel, low-energy solvent extraction schemes. [2.0 FTE]

**Materials and Molecular Research** **\$1,300,000**  
**Division**

**105. High Energy Oxidizers and Delocalized-Electron Solids**  
*N. Bartlett*

The program's main aim is the synthesis and characterization of new materials. The synthetic work tests models and theories which correlate physical properties (such as electrical conductivity) with chemical composition and structure. Emphasis is on the study of two-dimensional extended atomic networks such as those derived from graphite, layer-form boron nitride and their relatives. Electron-oxidation of such materials (with accompanying intercalation to form salts) generates durable and conductive materials (some better than aluminum). Chemical, stoichiometric, and structural requirements for the best conductivity are being defined. Layered materials can often be oxidized (and intercalated) electrochemically, the process also being reversible. Thus graphite may be reversibly converted by electrochemical means to a graphite flouride of approximate composition  $\text{C}_{2.5}\text{F}$ . This novel material, which could be important as a high-energy electrode, possesses a  $\pi$ -electron system which appears to be similar to that in pristine graphite. Physical and chemical studies are being applied to this and related materials to determine the structure and bonding changes which accompany the oxidation and reduction. Salts which are either proton conductors or flouride ion conductors, but not metallic, and which are resistant to oxidation, are being sought as solid electrolytes for use with metallic layer-material salts. [4.7 FTE]

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

The purpose of this program is to develop an understanding of the fundamental processes involved in catalytic conversion of carbon monoxide and hydrogen to gaseous and liquid fuels. Attention is focused on defining the factors which limit catalyst activity, selectivity, and resistance to poisoning, and the relationship between catalyst composition/structure and performance. To meet these objectives, a variety of surface diagnostic techniques (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 involved in carbon-monoxide hydrogenation. [6.0 FTE]

**107. Transition Metal Catalyzed Conversion of CO, NO, H<sub>2</sub>, and Organic Molecules to Fuels and Petrochemicals**  
*R.G. Bergman*

The central objective of this program is the discovery of new chemical reactions between organic compounds and transition metals, and the understanding of how these reactions work. Particular attention is paid to transformations that involve the most fundamental bonding changes (e.g., formation and cleavage of bonds between carbon, hydrogen, nitrogen, and oxygen), which occur in important large-scale transformations of organic compounds, such as those employed in industrial catalysis and stoichiometric organic synthesis. A recent discovery on this project was that a certain class of iridium complexes undergoes oxidative addition into the carbon-hydrogen bonds of completely saturated hydrocarbons (alkanes). This is the first example of this long sought C-H activation reaction, and research during the past year has been directed at understanding its scope and selectivity. Recently, methods for extending the iridium-based alkane activation chemistry to appropriately substituted rhodium complexes have been developed. Work is under way aimed at studying the properties of these different metal systems, understanding and comparing the mechanisms of the reactions, and developing methods for using this chemistry to convert alkanes into more useful, functionalized organic molecules. [2.6 FTE]

**108. Formation of Oxyacids of Sulfur From SO<sub>2</sub>**  
*R.E. Connick*

The research is aimed at understanding the fundamental chemistry of sulfur species formed from sulfur dioxide in aqueous solution and the chemical reactions of these species. The chemistry of these systems is of particular importance in the problems associated with atmospheric pollution by sulfur dioxide and the resulting formation of acid rain. Research has focused on the kinetics of the exchange of oxygen atoms between bisulfite ion and water, using the nuclear magnetic resonance of oxygen-17 for following the reaction. Results indicate a rate law consistent with exchange through formation of sulfur dioxide. The most intriguing finding is that there are two separate bisulfite species present, presumably the two isomers, which differ in the attachment of the proton to the oxygen or the sulfur. The latter species is about one-sixth as abundant as the former and does not exchange oxygens with water at a significant rate. A secondary and not closely related goal is to determine the factors controlling the rate of substitution reactions in the first coordination sphere of metal ions. Computer modeling of such systems is under way and some results for a two-dimensional model have been published. Work will be extended to three dimensions using a more sophisticated model for water. [2.0 FTE]

**109. Chemistry and Morphology of Coal Liquefaction**  
*H. Heinemann*

We are studying the catalytic gasification of graphite or char to produce methane and higher hydrocarbons. Within the last year it has been found that the apparent self-limiting step, namely the formation of a potassium phenolate group, can be circumvented by a simultaneous catalytic decomposition of the phenolate. It is intended to now look for better catalysts for this step and to improve rates and yields of hydrocarbon formation as well as to determine the mechanism for the formation of hydrocarbons heavier than C<sub>1</sub>. In the selective hydrogenation of

nitrogen-containing aromatics, work is under way to find methods for splitting out N as nitrogen or ammonia from partly-saturated aromatics. (If successful, this would provide leads for a low-temperature, low-pressure denitrification with low hydrogen consumption.) Simultaneously, catalytic mechanisms of hydrogen transfer from partially-saturated, nitrogen-containing ring compounds are being investigated. [1.2 FTE]

**110. Synthetic and Physical Chemistry**  
*W.L. Jolly*

The main objective of this project 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 which have analogs in the molecules chemisorbed on metal surfaces and in the intermediates of catalyzed organic reactions. Of particular interest are studies of metal cluster complexes, in which the ligand-metal interactions are very similar to those on metal surfaces. [11.5 FTE]

**111. Surface Chemistry—Application of Coordination Principles**  
*E.L. Muetterties*

Definition of the coordination chemistry of transition metal surfaces on a comparative basis with that of molecular metal complexes and molecular metal clusters is the research objective. Displacement reactions, supplemented with diffraction and spectroscopic data, will be used in elucidation of structural, bonding, and chemical features of the nickel and platinum metal surfaces with chemisorbed molecules. Initial studies focused on the chemisorption states of aromatic hydrocarbons, olefins, and acetylenes on nickel and platinum surfaces. Catalytic reactions of these molecules will be examined in an ultrahigh vacuum chamber equipped with an isolation cell. These catalytic reactions will be closely correlated with metal cluster research so as to obtain a precise comparison between homogeneous and heterogeneous catalysis. 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. [2.0 FTE]

**112. Electrochemical Systems**  
*J. Newman*

This program includes investigation of fluid flow and electrochemical transport, analysis of mass-transfer rates and current distribution, design of practical electrochemical systems, and investigation of corrosion processes. Coupled kinetic, mass-transfer, and fluid-flow phenomena are investigated in semiconductor electrode systems, with emphasis on the optimization of configurational and operating parameters of liquid-junction photovoltaic cells. [0.4 FTE]

**113. Organometallic Chemistry of Coal Conversion**  
*K.P.C. Vollhardt*

The basic program objective is to apply organometallic processes and techniques to the solution of problems concerned with the conversion of coal to liquid and gaseous fuels. The potential of novel organometallic systems as catalysts and photostorage devices is being explored. A series of experiments on trinuclear biscarbyne clusters as potential models for surface mediated carbon-carbon and carbon-hydrogen bond making and bond breaking processes has been completed. This work has led to the discovery of novel transformations in the coordination sphere of transition metal clusters including carbyne-carbyne coupling and decoupling, chalcogen induced degradation, and electrophilic substitution chemistry at the apical carbon. In addition, a novel thermally reversible photochemical vinyl-hydrogen activation has been observed with potential in photochemical storage devices. A new method for constructing fulvalene complexes has allowed the exploitation of unprecedented binuclear chemistry of homo- and heteronuclear transition metal derivatives. Several of these compounds have shown novel and distinct chemistry of relevance to catalysis and photochemical storage cycles. These systems are being investigated as potential models in heterogeneous Fischer-Tropsch polymerization and the activation of small molecules. The preparation and isolation of soluble, defined molecular systems has allowed structural and mechanistic information to be assembled in unprecedented material. [2.4 FTE]

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

**Chemistry Division** **\$234,000**

**114. Synthesis of Thermochemical Cycles**  
*W.M. Jones, E. Onstott, M. Bowman*

This research is directed to an understanding of the basic chemistry and engineering principles required to synthesize efficient thermochemical cycles for the production of hydrogen from water by the use of heat sources such as solar, nuclear fission, and nuclear fusion reactors. A general objective is to establish the criteria required for the development of this new technology and for the evaluation of worldwide programs. The research consists of the identification, initial evaluation, and preliminary development of different cycles through measurements of reaction rates, reaction yields, and thermochemical properties. Current studies include: (1) thermochemical cycles based on decomposition of metal sulfates and hydrogen iodide, where the recycle reagents are sulfur dioxide, water, iodine, and a rare earth dioxymonosulfate; and (2) evaluation of low temperature reactions in cycles based on decomposition of metal oxides and hydrogen iodide, where the recycle reagents are water, iodine, magnesium hydroxide, and an oxide of copper, iron, manganese, or cobalt. [1.4 FTE]

**Isotope and Nuclear Chemistry Division** **\$235,000**

**115. Labile SO<sub>2</sub> Complexes**  
*G.J. Kubas, G.D. Jarvinen, R.R. Ryan*

The basic chemistry of sulfur dioxide is being expanded with regard to its binding to transition metal complexes, enhancing its reactivity and promoting catalytic reactions. The ultimate

goal is development of new methods for scavenging SO<sub>2</sub> from flue-gases. Work includes synthesis and structural characterization of new SO<sub>2</sub> complexes and catalytic reactions of SO<sub>2</sub> with other small molecules. For example, SO<sub>2</sub> and NO<sub>x</sub> have been converted to sulfur, nitrogen, and water by hydrogen reduction over a Ru/alumina catalyst, and methods of catalyzing such reactions homogeneously are being investigated. A catalytic conversion using organometallic molybdenum sulfide complexes has been discovered in which hydrogen reduction of SO<sub>2</sub> to sulfur and water takes place under mild conditions. Reactions of SO<sub>2</sub> with transition metal hydride complexes are being studied in order to identify intermediates and mechanisms involved in hydrogen transfer to SO<sub>2</sub>, and insertion of SO<sub>2</sub> into a metal-hydride bond, a possible key step in hydrogenation, has been observed for the first time. As a spinoff of the above work, the first example of a molecular hydrogen complex, W(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>(eta<sup>2</sup>-H<sub>2</sub>) has been discovered, and its possible role in catalytic hydrogenation is under investigation. [1.5 FTE]

**Monsanto Research Corporation**  
**Miamisburg, Ohio 45342**

**MRC-Mound** **\$175,000**

**116. Fundamental Investigations Of Metal Hydrides**  
*R.C. Bowman, Jr., G.C. Abell, M.P. Guse*

The program objective is to obtain a fundamental understanding of the role of interstitial hydrogen on the electronic and structural properties of a host metal. Experimental techniques such as NMR, variable temperature x-ray diffraction, and thermal analysis are being used: (1) to evaluate specific properties of the electronic structure; (2) to determine the effect of host metal structure, hydrogen site occupancy, and alloy substitution on hydrogen diffusion; and (3) to study the ramification of phase transitions on the electronic structure of the metal hydrides. Among the hydrides under current investigation are the AB<sub>3</sub> compounds, zirconium and titanium based alloys both crystalline and amorphous, and the Laves alloys. Monte Carlo type calculations are used to correlate NMR lineshapes with hydrogen site occupancy. Quantum-mechanical calculations of the electronic properties of clusters of metal atoms with hydrogen interstitials are being used to describe additional experimental results. Short-range electronic structures are being explained using a localized electronics states model. [2.5 FTE]

**Oak Ridge National Laboratory**  
**Oak Ridge, Tennessee 37831**

**Chemical Technology Division** **\$310,000**

**117. Kinetics of Enzyme Catalyzed Processes**  
*E. Greenbaum, J. Woodward*

This research project is focused on understanding the fundamental chemical and physical mechanisms of enzyme-catalyzed reactions. The specific systems under investigation are the *in vitro* photosynthetic system composed of isolated chloroplasts, ferredoxin, and hydrogenase (CFH), and the enzyme-catalyzed conversion of cellulose to glucose. The CFH system is capable of the simultaneous photoproduction of hydrogen and oxygen when irradiated with visible light. Experimental progress includes the first measurements of the light saturation curves of

biophotolysis of water and the first demonstration of the simultaneous photoproduction of hydrogen and oxygen by immobilized chloroplasts, ferredoxin, and hydrogenase. The result is that the analytical shapes of the light saturation curves are not the same. A higher light intensity is required to saturate the hydrogen curve. These results challenge the Z-scheme concept of photosynthesis. A cellulase enzyme system is being investigated for the conversion of cellulose. An immobilized enzyme has been shown to maintain long-term stability and high activity for this application. [3.0 FTE]

**Chemistry Division** **\$2,183,000**

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

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

Research is conducted to derive an understanding of the principles controlling homogeneous and heterogeneous chemical processes to the extreme conditions (pressure-temperature-compositions) encountered in technological and natural systems. Advancement in techniques and in existing unique equipment will continue to be emphasized in studies of the reaction types: association, ionization, oxidation-reduction, hydrolysis, hydration, complexation, and precipitation. Species identification, thermodynamic properties, and equilibrium stability information are obtained, but new emphasis will be placed on structural and detailed quantitative information from neutron and Raman scattering research in collaboration with other programs in the Division. The future goals of the group include extension of the P-T-X conditions attainable in studies of excess Gibbs energies and enthalpies for important electrolyte systems, as well as definitive work on conductivities, electrochemical cells, and solution flow calorimetry. New techniques will be developed for studies of volumetric properties, absorption spectrophotometry, Raman spectroscopy, and neutron scattering. Results will contribute to the advancement in theories and models for water and its solutions, as well as provide a basis for detailed descriptions of the chemistry for systems important to steam generation, nuclear coolants, geochemical and hydrothermal processes, waste transport, nuclear accident assessment, and supercritical fluid processing. [5.5 FTE]

**119. Heterogeneous Catalysis Related to Energy Systems**

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

This program involves two related activities. In the first, the technique of low energy 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. The information content from alkali metal ions ( $\text{Li}^+$ ,  $\text{K}^+$ ) exceeds that from inert gas ions because of their lower neutralization probability. These methods have been applied to study surface reconstruction of Au(110), bonding geometry and ordering of O, C, N, and S overlayers on Mo(001), and surface structure of amorphous  $\text{Fe}_{80}\text{B}_{20}$  ribbon. The second activity, under initial development, will examine surface adsorption on metal sulfide surfaces in ultrahigh vacuum by electron spectroscopy and by thermal desorption spectroscopy. A sample transfer system will permit

the sample to be moved to an adjoining high pressure cell, which will be used for monitoring hydrodesulfurization and hydrogenation 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. [2.3 FTE]

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

*M.L. Poutsma, B.M. Benjamin, L.L. Brown, E.W. Hagaman, R.R. Chambers*

The objective of this program is improved understanding of the chemical structure and reactivity of coal. The approach involves chemical and spectroscopic techniques, and interpretation of results from studies with coal is aided by parallel studies with appropriate model compounds. The key spectroscopic technique used for native and chemically modified coals is solid-state CP/MAS  $^{13}\text{C}$  NMR. Current emphasis is on developing reliable techniques for quantification, and a recent initiative is aimed at performing double cross polarization experiments. Diagnostic reactions for structural features in coal are being developed, including the selective derivatization of coal carbanions based on differences in acidity of C-H bonds, and the identification and quantitation of aliphatic substituents and linking groups in coal by acid-catalyzed transalkylation. The effect of diffusional restraints on the thermal reaction pathways of key structural units in coal is investigated by the use of model compounds covalently attached to the surfaces of inert solids. [8.3 FTE]

**121. Molten Salt Catalysts For Clean Fuel Synthesis**

*G.P. Smith, A.C. Buchanan, III, A.S. Dworkin, S.P. Zingg*

This research is directed at the mechanisms by which molten halide salts hydrocrack coal model compounds. Our study of the important redox functionality of antimony trichloride-based catalysts continues and is now focused on the formation and decay reactions of radical cations and dications of polycyclic arenes and heteroaromatics in these media. We recently demonstrated that redox functionality is an important component of the catalytic activity of gallium trichloride in which the uncomplexed gallium(I) ion provides the reduced state. We will soon begin studies to determine whether or not aluminum chloride and the chloroaluminates possess a redox functionality. These investigations are based on the application of *in situ* spectroscopies (NMR, ESR, and fast optical) and electroanalytical methods combined with quench and separation procedures. Highly purified salts are used in controlled atmosphere glove boxes and closed systems. [4.7 FTE]

**Pacific Northwest Laboratories  
Richland, Washington 99352**

**Dept. of Chemical Technology** **\$470,000**

**122. Hydrogenation Mechanisms of Coal**

*J.A. Franz, R.D. Barrow, D.M. Camaioni*

This program is basic research directed at 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 deter-

mined, with absolute rates determined by kinetic laserflash spectroscopy for key atom transfer reactions. The cyclization of ortho-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. [2.0 FTE]

### 123. *Thermochemical Conversion of Solid Wastes Into Liquid Fuels*

*D.A. Nelson, P.M. Molton, R.T. Hallen*

The purpose of this research is to determine the reaction mechanisms involved in biomass liquefaction in aqueous media at elevated temperatures. Due to the complexity and variability of the composition of biomass, the liquefaction of pure cellulose is now being studied. Fast heating and cooling during liquefaction has helped determine which components are initially produced from cellulose. For instance, biacetyl appears to be formed from erythrose which is a retro-aldol product of glucose. Thus, many of the reactive intermediates formed during liquefaction act as precursors for other products with time. The use of alkaline catalysts under liquefaction conditions was to shift the mechanism from one involving aqueous pyrolysis (predominant furan formation) to one incorporating aldol and related condensations. Incomplete mixing of the alkaline catalyst allowed both mechanisms to operate during liquefaction with fast heating and cooling rates. [1.8 FTE]

### Sandia National Laboratories Albuquerque, New Mexico 87185

Dept. of Radiation and Surface Physics      \$250,000  
Research

### 124. *Reaction Kinetics Over Single Crystal Catalysts* *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<sub>2</sub> 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., S), neutral (e.g., Ag, Cu), or electropositive (e.g., K), onto a catalytically active single crystal substrate (e.g., Ni, Ru, Rh). 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. These reactions include CO and CO<sub>2</sub> methanation, alkane hydrogenolysis, and olefin hydrogenation. [1.6 FTE]

Surface Chemistry and Analysis Division      \$100,000

### 125. *FTIR Catalyst Studies*

*D.M. Haaland*

Fourier transform infrared spectroscopy (FT-IR) is being used to study surface catalyzed reactions over supported metal catalysts. In particular, the reaction of hydrogen and carbon monoxide to form methane and higher hydrocarbons is of interest. Infrared spectroscopy allows the reactant molecules on the surface to be used as effective probes of the local environment to determine modifier-adsorbate, adsorbate-adsorbate and metal-adsorbate interactions. Therefore, FT-IR can be used to investigate the role of modifiers (promoters and poisons) on both the adsorbed reactants and the kinetics of their reaction to form methane and higher hydrocarbons. The presence or absence of long-range interactions between modifiers and adsorbants will be determined. In addition, FT-IR coupled with temperature programmed desorption and temperature programmed reaction will be used to measure relative strengths of adsorption, rates of reaction, and reaction products formed on catalysts both with and without surface modifiers. [0.8 FTE]

### Solar Energy Research Institute Golden, Colorado 80401

Division of Research

\$156,000

### 126. *Basic Research in Synthesis and Catalysis* *J.C. Smart, D.L. Dubois, C.J. Curtis*

This basic research program involves the synthesis, characterization, and reaction studies of transition metal coordination complexes and organometallic compounds for the photoconversion of N<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, and related substrates to fuels and chemicals. It includes structural, spectroscopic, and mechanistic studies with the goal of understanding the interrelationship of molecular geometry, electronic structure, and catalytic reactivity in photochemical and photoelectrochemical transformations. Designed organometallic synthesis has yielded new bi- and trimetallic complexes with bridging fulvalene, *s*- and *as*-indacene, and trindene ligands of Ti, Zr, Ta, Mo, and Mn. Spectroscopic and photochemical studies of Co and Ni metallofulvalene and metalloindacene complexes is contributing to an understanding of their electronic structures and the potential utility of their low-lying excited states in photocatalysis. Photoelectrochemical N<sub>2</sub>-fixation studies involve the synthesis and characterization of surface bound polymer-pendant phosphine molybdenum(O) dinitrogen complexes using combined FT-IR and electrochemical techniques. [1.5 FTE]

## Separation and Analysis

Ames Laboratory  
Ames, Iowa 50011

Processes and Techniques

\$1,030,000

### 127. *Hydrometallurgical Processing* *R.G. Bautista*

The development and understanding of hydrometallurgical methods of recovering metals to include: (1) dissolution (leaching); (2) separation and concentration (ion exchange, solvent

extraction, and membrane separation); and (3) metal reduction from solutions (cementation, precipitation, and electrolysis) based on the equilibria, mechanisms, kinetics, and transport properties of the chemical reaction system are the related activities which are the principal objectives of this research program. The research projects presently being completed include: (1) the prediction of the concentration changes of the various species in solution during the dissolution of pyrrhotite and pentlandite by ferric sulfate and sulfuric acid; (2) the characterization of the solvent extraction mechanism of gallium in the system  $\text{GaCl}_3\text{-AlCl}_3\text{-HCl-H}_2\text{O}$ -tributyl phosphate; and (3) the electrochemical dissolution of chalcopyrite carried out in a liquid fluidized bed electrochemical reactor as a means of separating the copper, iron, and sulfur by a series of oxidation/reduction reactions. [2.0 FTE]

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

This effort is devoted to the systematic observation of spectroscopic phenomena, with the ultimate goal of utilizing these observations for devising new spectroscopic analytical concepts that offer promise of solving singularly difficult analytical problems that either exist now or are likely to arise in the future in the various fields of energy generation (the conversion of coal to liquid and gaseous fuels, solid state materials research, and in environmental pollution). Emphasis is being placed 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 processes from x-ray and laser beams to trace constituents in solid materials, leading to optical emission (e.g., x-ray or laser excited optical luminescence); (3) selective energy transfer from gaseous metastable species to trace level gaseous organic or inorganic constituents, with the intent to devise new analytical concepts; and (4) photoacoustic spectroscopy analytical techniques. [4.7 FTE]

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

A major effort is under way to improve our new method of ion chromatography, 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. An improved statistical theory of chromatography has been formulated to correct some inadequacies of prevailing theories and provide a better foundation for chromatography. [2.0 FTE]

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

The general objective of this research program 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 being 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. [2.4 FTE]

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

This program is aimed toward the development of 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. Specific areas of concern include: (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; and (5) laser-induced chemiluminescence for specific gas analysis. Investigations include the fundamental principles behind the measurements, the evaluation of the analytical potentials, and the demonstration of the analytical method in representative samples. [6.0 FTE]

## Argonne National Laboratory Argonne, Illinois 60439

Division of Chemistry

\$1,330,000

### 132. Separations Science Related to Nuclear and Hydrometallurgical Technology *E.P. Horwitz, P.R. Danesi, H. Diamond, D. Kalina, L. Kaplan*

This program has as its objectives the development of new separation processes and energy-efficient techniques applicable to nuclear and hydrometallurgical technologies and the elucidation of the basic chemistry involved. Major areas of investigation are: (1) the synthesis and characterization of new extractants for metal ion separation by liquid-liquid extraction (LLE) and supported liquid membranes (SLM); (2) the basic physical chemistry of supported liquid membranes, with emphasis on the various factors which influence the permeability rates of metal ions; and (3) the evaluation of the separation potential of new extractant and SLM systems, with emphasis on developing 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. [8.0 FTE]

**133. Study of Atmospheric Trace Gases By Mass Spectrometry**  
*C. Stevens*

The carbon isotopic compositions of atmospheric methane and natural and anthropogenic sources of methane are being measured to establish the relative distribution of these sources. In addition, we are collaborating with Dr. R. Rasmussen of the Oregon Graduate Center in analyzing the isotopic composition of methane in old air samples collected in both hemispheres since 1978. Changes in the composition reflect changes in the fluxes of enriched or depleted  $^{13}\text{C}$ -methane. The purpose of these measurements is to provide clues for causes of an increasing concentration of atmospheric methane, whether it is caused by increasing source fluxes or a decreasing rate of removal from the atmosphere. The results of this study bear on the extent of the methane contribution to the so-called greenhouse effect and its effect on future climate changes. They also provide important quantitative knowledge of anthropogenic source fluxes of  $\text{CH}_4$  and the global concentration of atmospheric OH radicals. [1.3 FTE]

**134. Separations of Coal Macerals and Other Fossil Fuels**  
*R.E. Winans, G.R. Dyrkacz, C.A.A. Bloomquist*

The major objective of the project is to develop new methods for the separation of coal macerals. This program has been able to reduce the complexity of coal science by the separation of coals into their maceral constituents using density-gradient centrifugation. Characterization of these maceral concentrates has led to a better understanding of their role in coal chemistry. More efficient methods of separation are being explored which exploit differences in surface properties. [2.7 FTE]

**Brookhaven National Laboratory**  
Upton, New York 11973

**Dept. of Applied Sciences** **\$300,000**

**135. Specific Molecular Property Detectors For Chromatographic Analysis**  
*J.S. Gaffney, E.J. Premuzic*

This research effort is developing novel specific molecular property detectors for use in gas and liquid chromatography. Detection schemes are devised which 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 program is currently developing monitoring devices for specific hydrocarbons and hydrocarbon classes. Use of vacuum-ultra violet (130-300nm) 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 (NSLS) 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), as well as photothermal laser spectroscopies, are also being investigated as selective and sensitive devices for chromatographic detection. [1.8 FTE]

**136. Cyclic Separations Process Research**  
*F.B. Hill*

The purposes of this program are to obtain an understanding of the characteristics and basis of operation of cyclic separation processes as a class and to explore the feasibility of using these processes to perform specific separations important in the energy field. The cyclic processes of interest include pressure and temperature swing adsorption, parametric pumping, cycling zone adsorption, and various forms of preparative chromatography. Applications presently under study involve hydrogen isotope separations of concern in fusion reactor fuel processing and in heavy water reactor technology, and helium extraction from natural gas. Future work will include applications such as hydrogen recovery and purification and ion exchange separations useful in radwaste applications. Elements of the program include development of the theory of cyclic processes, measurements of equilibrium and kinetic properties of selected fluid-solid separation systems, measurement of the characteristics of cyclic separation processes employing these systems, and process design and evaluations studies. [1.2 FTE]

**Dept. of Chemistry** **\$200,000**

**137. Applications of Nuclear Methods to Analysis**  
*G. Harbottle, E.V. Sayre, R.W. Stoerner*

This program is concerned with the extension and improvement of nuclear methods of elemental analysis, particularly methods that permit the determination of many components (including trace impurities) quickly and efficiently, and with the development of computer-based multivariate statistical analysis which will permit the efficient and effective analysis of large assemblages of such analytical data. These methods are being applied to a wide variety of materials for which geographic origins are of significant interest. The effects of geochemical processes on trace element patterns are being investigated in several natural materials and artifacts made from them. Studies of the accuracy and precision of standardization in activation analysis are an important part of the project. The improved proportional counter method for carbon-14 measurement in samples as small as 10 mg is being applied to marine sediments in an attempt to account for the carbon dioxide inventory of the world. [2.7 FTE]

**Dept. of Physics** **\$350,000**

**138. Analytical Techniques With Synchrotron Radiation and Ion Beams**  
*K.W. Jones, H.W. Kraner, B.M. Gordon*

This program develops new analytical techniques for elemental analysis using synchrotron radiation from the National Synchrotron Light Source. Equipment is being designed and fabricated to produce a focused x-ray beam with a spatial resolution in the neighborhood of 10 micrometers. Techniques for precise trace element measurements with minimum detectable limits approaching  $10^{-9}$  g/g are being developed concurrently for both bulk and microanalysis. 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 identification is supported by the use of nuclear ion-beam analysis, which makes available complemen-

tary analytical techniques that are used to corroborate and extend the synchrotron radiation results. [4.0 FTE]

**EG & G Idaho, Inc.**  
**Idaho Falls, Idaho 83401**

**Idaho National Engineering Laboratory**      **\$120,000**

**139. Negative Ionization Mass Spectrometry**  
*J.E. Delmore*

This program is studying two ionization processes for application to negative ion mass spectrometry: negative surface ionization and electron capture. Surface ionization studies are focused on systems where the species of interest is chemisorbed on a low work function surface, followed by thermal desorption. To date, ions studied by this method include Cl, Br, I, BO<sub>2</sub>, CN<sup>-</sup>, CNO<sup>-</sup>, and H<sup>-</sup>. Ionization efficiency has been increased by several orders of magnitude using this technique. 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 a cycloidal orbit to reduce the kinetic energy to thermal values. The thermalized electrons are readily captured by gas molecules to form negative ions, without the high pressure system otherwise required for electron capture mass spectrometry. Refinement of both the experimental model and instrumentation is the major thrust of the program for the next year. [1.0 FTE]

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

**Physics Division**      **\$177,000**

**140. The Formation and Properties of Complexes of Helium and Hydrogen Isotopes**  
*R.D. Taylor*

The conditions for formation and the properties of a metastable, bound-state complex of <sup>3</sup>He and tritium are under study. T<sub>2</sub> decays with a half life of 12.3 years, ultimately producing a pair of <sup>3</sup>He atoms. However, vapor pressure time measurements show that the <sup>3</sup>He formed in liquid T<sub>2</sub> is retained in the liquid in an amount far exceeding the ordinary solubility. This complex, once formed, is found to be unstable in the gas phase, but it is virtually stable in liquid or in solid tritium. Preliminary data for solid T<sub>2</sub> at 20.0 K suggest that the newly formed <sup>3</sup>He is also bound. The electrical conductivity of solid T<sub>2</sub> containing the complex shows an initial decline of about a factor of three from the conductivity of the liquid. After a few days, this conductivity is about 100 times less. A new cell has been built that will allow pressure buildup measurements of liquid or solid T<sub>2</sub> without the complication of gas phase corrections. Other time-temperature measurements to characterize the complex include magnetic susceptibility and compositional studies of successive portions of gas removed from the cold cell. [1.3 FTE]

**Monsanto Research Corporation**  
**Miamisburg, Ohio 45342**

**MRC-Mound**      **\$775,000**

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

This program is concerned with the investigation of 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 with an emphasis on macrocyclic complexants and toward the development of two-phase isotope exchange processes for practical separations. The liquid thermal diffusion work is directed, in part, toward developing a basic understanding of the behavior of liquid phase thermal diffusion columns and, in part, toward gaining and interpreting experimental information about the isotopic thermal diffusion factor in the liquid phase. [3.6 FTE]

**142. Atomic and Molecular Properties and Their Relationships to Separation Processes**  
*W.L. Taylor, G.T. McConville, R.W. York*

The objective of this research is to investigate the physical properties of isotopes and their mixtures. To obtain a more complete understanding of gaseous mixtures of hydrogen isotopes, in particular, the mechanisms for isotopic exchange in such mixtures, measurements of the formation of DT in mixtures of D<sub>2</sub>+T<sub>2</sub> are being made as a function of pressure, initial T<sub>2</sub> concentration, and temperature. The interaction with D<sub>2</sub> is very complex, and the presence of excited state molecules plays a definite part in the reaction. Such information will be useful in design criteria for fuel handling systems in the controlled-thermonuclear power program. Total cross sections are being measured for the permanent gases with supersonic molecular beams. The data are analyzed to yield the fundamental interactions of the colliding species. The temperature range of diffusion measurements in binary gas mixtures is being extended to ~2500°C by means of a Ta/W diffusion cell operating in a vacuum furnace. The thermodynamics of the thermal diffusion process is under study in a "swing separator" instrumented with thermistors *in situ* and real time analysis of the separation process. Ortho- and para-deuterium are being separated in a cryogenic adsorption column and will be made available to the Stable Isotope Inventory Program. [4.2 FTE]

**Oak Ridge National Laboratory**  
**Oak Ridge, Tennessee 37831**

**Analytical Chemistry Division**      **\$1,352,000**

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

A rapid growth has occurred in recent years in particle sputtering as a means for producing atoms and ions for mass spectral analysis. More recently it has been observed that secondary ion mass spectrometry (SIMS) offers a means of studying organic as well as inorganic materials. The major thrust of our research program has shifted in this direction, and our approach to organic SIMS has been to interface an in-house developed secondary ion source with a tandem three-sector mass spectrometer. This combination will be used to investigate the chemistry and physics of secondary ion emission from both volatile and involatile organic species. In inorganic SIMS, we plan to investi-

gate laser induced resonance ionization of sputtered neutrals using a recently acquired microbeam instrument that is now being modified for these studies. Fundamental information concerning the sputtering process will be obtained since resonance ionization allows one to probe the excited electronic states of neutral atoms ejected during a sputtering event. This information will be used to refine the theory of sputtering phenomena including secondary ion emission which is the basis for SIMS. [2.0 FTE]

**144. Mass Spectrometry R&D For Organic Analyses**  
*G.L. Glish, P.J. Todd, E.H. McBay, S.A. McLuckey*

This task consists of studies in two general areas of organic mass spectrometry. Both are experiencing rapid growth in popularity as analytical techniques even though much is yet to be understood about the underlying chemical and physical principles. These areas are: (1) mass spectrometry/mass spectrometry (MS/MS); and (2) desorption ionization (DI). The main thrust of this task is to investigate the chemical and physical phenomena associated with these areas to further the understanding and therefore make the application of MS/MS and DI easier for the general mass spectrometrists. The studies of these areas are in many ways complementary. MS/MS is a very good tool to study gas phase ionic structures and thus can be used to help elucidate chemical processes which occur during DI. Conversely, DI can be used to generate unique types of ions which can be used to assist in extending the understanding of MS/MS. Of particular interest is the gas phase ion chemistry and physics involved in MS/MS. Studies in these areas will not only better the understanding of the basic phenomena in MS/MS, but also the basic processes in mass spectrometry in general. [2.2 FTE]

**145. Advanced Spectroscopic Methods For Chemical Analysis**  
*L.D. Hulet, J.M. Dale, T.M. Rosseel*

The objective of this research is to explore new physical phenomena for applications as spectroscopic methods. Positron spectroscopy is being evaluated for characterization of surfaces and bulk materials, doing chemical analyses, surface area measurements, and solid state defect studies; the monoenergetic positron sources developed earlier in this project and the ordinary fast sources are being used. Ions from the EN Tandem Accelerator and the Holifield Heavy Ion Facility are being used to induce heavy ion x-ray satellite emission spectra (HIXSE) for studies of valence states of metal alloys and other materials. X-ray diffraction and electron microscopy are being applied to special analytical problems dealing with laser research. The positron and heavy ion methods are being developed for use in other programs, such as surface modification, the High Temperature Materials Laboratory (HTML), and mass spectrometry research. Other groups at State University of New York, Fredonia, Duke University, and the University of Missouri are also collaborating with this program. [2.8 FTE]

**146. Research Development and Demonstration of Advanced Chemical Measurement Techniques**  
*H.H. Ross, J.M. Ramsey, L.N. Klatt, W.B. Whitten, J.P. Young*

New spectroscopic and instrumentation techniques are being developed that have the potential of meeting critical measurement needs in the analytical community. A new project that

employs lasers and phase conjugate optics may lead to a whole new concept in laser scanning systems. Time resolved fluorescence spectroscopy is being developed for a broad range of important analytical applications. Fourier transform microwave spectroscopy is being pushed for the rapid quantitation of complex organic and inorganic mixtures. A new computer system is being programmed to collect data for this project as well as carry out the fast Fourier transform processing that is needed. Ongoing studies of laser excited optogalvanic spectroscopy will be extended to diagnostic studies of plasmas used in chemical vapor deposition experiments. We are starting a new research program that exploits robotics in analytical chemistry. [3.8 FTE]

**147. Mass Spectrometric R&D For Inorganic Analyses**  
*R.L. Walker, H.S. McKown, D.H. Smith, D.L. Donohue, D.E. Goeringer*

The objective of this research is to improve isotopic ratio mass spectrometry and to extend its areas of application. Areas in which improvement is being sought include instrumentation and methodology, precision of analysis, and elemental specificity. Our laboratory houses state-of-the-art, high sensitivity, multi-staged mass spectrometers to provide high quality isotopic ratio measurements on extremely small samples (~1 ng). Low-level separations techniques are carried out in a Class 100 clean room and isotope dilution is used extensively for quantitation. Resonance ionization mass spectrometry has been applied successfully to uranium and plutonium. Sensitivity and precision are quite good (10 ng samples, 0.5% standard deviation). Spectral characterization of six elements (Pu, U, Th, Cm, Np, Am) was carried out in the 580-600 nm range. A comparison of pulsed versus continuous wave laser ionization will be carried out next. A double spike (internal standard) of plutonium has been studied using NBS SRMs; it affords an improvement in precision of a factor of five over conventional techniques. A preliminary evaluation of our channel electron multiplier array (position sensitive) detector has been completed. [2.3 FTE]

**Chemical Technology Division** **\$1,424,000**

**148. Chemical and Physical Principles in Multiphase Separations**  
*C.H. Byers, R.M. Wham, C.D. Scott*

Fundamental chemical engineering investigations include new concepts and basic understanding of multiphase separation methods. Fluidized and expanded beds are stabilized by the imposition of an electric field, thus exhibiting the desirable sorption characteristics of fixed beds, while the pressure drop is approximately half the fixed bed. The applicability of this principle to a novel method for moving bed sorption is under study. Mass transfer enhancement in dispersed-phase systems by forcing the oscillation of small droplets in a continuous medium is being investigated. Preliminary results show that droplet motion can be forced by an oscillating electric field. A study to investigate separation phenomena associated with the distribution of a solute between a liquid and solidified (frozen) solvent has been initiated. Preliminary results indicate that chromatographic separation of selected solutes is possible. [5.3 FTE]

**149. Chemical Separations For Tritium**  
*P.W. Fisher*

This program studies fundamentals of tritium separation techniques needed for fusion and fission reactor systems. Recent studies have been concerned with tritium sorption from liquid lithium by metallic getters such as yttrium and yttrium alloys. Tritium diffusion rates in both solid and composite metals were investigated, and a correlation was developed which describes the behavior of composites. More recent studies have been directed at the interactions of tritium and tritiated water molecules at solid surfaces. These studies will investigate the roles of sorption, exchange reaction, desorption, and bulk diffusion processes on tritium uptake and release from surfaces. More fundamental understanding of these phenomena will be useful to a number of problems in fusion and fission reactor systems, such as contamination of surfaces, retention of tritium following accidental releases, exchange of molecular tritium with the more hazardous oxide, and decontamination of used components. [1.4 FTE]

**150. *The Chemistry of Solvation Applied to Separations***

*J.E. Mrochek, H.D. Cochran*

Solvent-solute interactions (solvation) in both ionic and non-ionic media are of paramount importance to the understanding of many separation methods. This program investigates, in a systematic and fundamental manner, both short- and long-range solvation effects in mixed media. Current studies are directed at selected aprotic and supercritical solvents. Spectroscopic measurements, including both ultraviolet and nuclear magnetic resonance (nmr) relation techniques, are used to study both bound (inner) and bulk (outer) solvent molecules, and the results are related to thermodynamic properties. The studies are currently focusing on inorganic chloride solutes which have not been investigated extensively in the past, but have potential important applications. The studies with aprotic media are directed at speciation of complexes and modifications caused by introduction of known quantities of water into the systems. Studies under supercritical conditions are attempting to relate the heretofore empirical binary interaction parameter to an intermolecular potential function (e.g., Lennard-Jones potential). Subsequent studies will investigate polar solvents where the Stockmayer potential is appropriate. The results of these studies will increase our understanding of solute-solvent interactions, improve our predictive capabilities, and eventually be useful to a number of separation processes. [3.7 FTE]

**151. *Chemistry of Actinides and Fission Products***

*L.M. Toth, D.J. Pruett*

The chemistry of actinides and of fission products is investigated with emphasis on the properties that affect separation and partitioning in the nuclear fuel cycle. The broad scope of subjects includes: (1) photochemical studies; (2) the structures and properties of polymer materials; (3) solvent extraction and co-extractions, and (4) the induction times and precipitation in pseudo stable process and waste streams. Recent studies have concentrated on the solvent extraction of heptavalent technetium and rhenium in nitric acid systems with and without uranium, and on the photochemical reduction of heptavalent technetium to the V and IV states in nitric and hydrochloric acids. New research will include the photochemistry of low temperature uranium and plutonium frozen solutions or salts and the catalytic effects of Pu(IV) on actinide redox reactions. [3.0 FTE]

**Chemistry Division**

**\$690,000**

**152. *Chemical and Structural Principles in Solvent Extraction***

*J.H. Burns, C.F. Baes, Jr.*

The purpose of this research is to obtain basic information about solvent-extraction systems that may lead to improved processes for recovery of strategic materials for national energy needs. The approach is to investigate known successful processes with the aim of understanding, on a molecular level, the mechanism by which they operate, and to determine which variables of reactivity and structure are important to their success. The structures of solvent-extraction complexes in the solid state and in solution are being studied by the methods of x-ray diffraction and nuclear magnetic resonance. Among the systems being analyzed are those involving the extraction of uranium by organophosphorus ligands and those of alkaline earths by macrocyclic ethers. The structural information obtained is being used to develop criteria for solvent extraction which will have general applicability. These criteria are being used in the design of more effective extraction reagents for the actinides and could provide a guide for the development of new techniques for the separation of other metals. [1.8 FTE]

**153. *Chemical Separations By Complexation Phenomena***

*W.J. McDowell, B.A. Moyer*

Basic scientific understanding of methods for separating mixed elements, compounds, or aggregate materials is being obtained by systematic and fundamental studies of equilibria and mechanisms and of the properties of the components in selected separations systems. The present emphasis is on solvent extraction and ion exchange systems, which are well defined and of widespread concern. A major aim is understanding of the relationship between reagent structure and selectivity for particular ions or molecules, so that agents can be designed for improved selectivity, kinetics, and phase behavior. Multidentate extractants, including chelating and macrocyclic compounds, are emphasized because their known complex-forming behavior gives basis for designing specificity into reagents. Detailed studies include: (1) the effects of a range of functional groups when they are attached to carrier molecules or resin skeletons; (2) synergistic combinations of different functions; and (3) elucidation of the structures of adducts of metals with ligands that are known to be selective. [3.7 FTE]

**Pacific Northwest Laboratories  
Richland, Washington 99352**

**Dept. of Biology and Chemistry**

**\$140,000**

**154. *Fundamental Phase Partitioning in Supercritical Fluid Chromatography***

*R.D. Smith, B.W. Wright, H.R. Udseth*

The goal of this program is a fundamental understanding of the kinetic and thermodynamic constraints upon partitioning of a solute between a supercritical fluid and a supported phase. The program 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 equilib-

rium sampling, and various optical techniques. The program is directed at gaining an understanding of chromatographic processes for polar and mixed supercritical fluid and solute systems and the kinetic and thermodynamic limitations upon separations in supercritical media. Experimental results are being compared with both theoretical methods for prediction of fluid phase solubilities and actual chromatographic separations for model systems, with the aim of identifying critical parameters for the development of improved chromatographic systems. [1.0 FTE]

**Dept. of Radiological Sciences** **\$700,000**

**155. Laser-Based Analytical Techniques**  
*B.A. Bushaw, B.D. Cannon, T.J. Whitaker*

The objective of this program is to develop and evaluate ultrasensitive and highly selective laser-based analytical techniques. Photon correlation spectroscopy has been used to enhance the detection of Na, Rb, and Sr isotopes. Both photon burst and time interval distribution analysis have been used for single atom counting. The observed detection limits, 10 atoms per second crossing the laser beam or about  $0.1 \text{ atom/cm}^3$ , are governed by nonstatistical noise behavior of the photon counting electronics. Time correlation filtering of the detection of multiple photons from a single atom, combined with single frequency dye laser excitation, may provide resolution better than the natural Lorentzian lineshape. Isotopic selectivities one to two orders of magnitude better than observed in the normal fluorescence spectra have been demonstrated. Current efforts are directed toward extending these techniques to other elements and applying them to the analysis of discrete samples. A vacuum graphite furnace, similar to that used for flameless atomic absorption analysis, is to be used as an atomization source for many sample types. Other species may be observed by supersonic beam sampling of plasma discharges. Metastable states, formed in the plasma, are of particular interest for the detection of noble gases and other spectroscopically difficult elements. [1.4 FTE]

**156. Analytical Mass Spectrometry Research**  
*R.L. Gordon, J.M. Kelley, D.M. Robertson, J.J. Stoffels*

This task develops new knowledge and techniques to extend the application of mass spectrometry to problems in chemical and isotopic analyses. The task: (1) elucidates physicochemical mechanisms responsible for efficient ion production in isotopic analysis by surface ionization mass spectrometry; (2) develops methods for the control of surface work function of ion sources; (3) develops techniques for application of mass spectrometry to real-time analysis; and (4) establishes new ionization techniques. Surface analytical tools are used to establish physical and chemical properties of surface ionization sources and to identify chemical pathways responsible for ion production. The direct-inlet technique for real-time mass spectrometry uses innovations in ion sources, mass separators, and ion detectors. Laser-assisted ionization is being developed for new mass spectrometry ion sources. [3.3 FTE]

**157. Analytical Atomic Absorption Spectrometry Research**  
*D.L. Styris, J.H. Kaye*

This program elucidates experimentally the mechanisms that control sample vaporization in furnace atomic absorption (FAA) spectrometry. Vaporization models that are developed 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 presently 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 determine spatial distributions of gaseous species within the furnaces. [1.3 FTE]

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

**Dept. of Laser R & D** **\$150,000**

**158. Laser Based Analytical Methods**  
*A. Owyong, A.V. Smith, J.P. Hohimer, T.D. Raymond*

This research is directed toward the development of new, highly sensitive, species-specific laser-based analytical techniques with capabilities beyond the reach of conventional methods of analysis. To this end our program emphasizes: (1) the determination of the utility and limitations of newly developed laser-based techniques (such as multiphoton ionization spectrometry, MPIS) in analytical applications; (2) the integration of such techniques with more conventional methods of analysis (such as mass spectrometry) to provide analytical capabilities of increased dimension; and (3) the exploration of entirely new laser-based concepts having potential utility for analytical applications. This year we are performing a direct comparison between laser ionization and electron beam ionization methods for TOF mass spectrometry. We are also exploring the use of laser ionization methods for rotational-vibrational spectroscopy and the use of laser sources to enhance the utility of field-ionization mass spectrometry. [1.0 FTE]

**Chemical Engineering Sciences**

**Lawrence Berkeley Laboratory**  
**Berkeley, California 94720**

**Applied Science Division** **\$239,000**

**159. Turbulent Combustion**  
*F. Robben, R.K. Cheng, L. Talbot*

The effect of fluid mechanical turbulence on combustion is being studied experimentally for premixed fuel/air conditions in two idealized flow configurations: (1) turbulent boundary layer over a strongly heated wall where lean combustion occurs;

and (2) an unconfined v-shaped turbulent flame. Density and velocity fluctuations and several of their cross correlation parameters are measured, using techniques based on laser Rayleigh scattering and laser Doppler velocimetry. These measurements are useful to characterize the features of the flame structures and their effects on the turbulent flow field. The initiation and development of combustion in the heated boundary layer are found to be dominated by the large-scale turbulence structures. Measurements of Reynolds stress in the v-shaped flame have shown that a mean-gradient transport model for production of turbulent kinetic energy is not appropriate for these flames. [2.5 FTE]

**Materials and Molecular Research Division** **\$146,000**

**160. 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. In this context, "efficient" refers to optimum use of raw materials and to conservation of energy. Since the variety of technologically-important fluid mixtures is extremely large, it is not possible to obtain all desired equilibria from experiment. Therefore, the objective of this research is development of molecular thermodynamics for interpretation and correlation of selected phase-equilibrium data toward reliable general prediction of phase equilibria for engineering. The correlations are expressed through semi-theoretical physico-chemical models in a form suitable for computer aided design. In this research, particular attention is given to those systems that are of primary interest in energy-related industries, especially those concerned with fossil fuels and fossil-fuel-water mixtures. Development of molecular thermodynamics calls for a combination of theoretical, computational, and experimental work. Further, it demands simultaneous awareness of progress in molecular science and of realistic requirements for engineering design. [2.1 FTE]

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

**Theoretical Division** **\$73,000**

**161. Thermophysical Properties of Mixtures**  
*J.J. Erpenbeck*

Evaluation of the thermophysical properties of mixtures of particles that interact through the hard-sphere potential has been initiated, using equilibrium techniques of Monte Carlo (MC) and molecular dynamics (MD) as well as non-equilibrium molecular dynamics (NEMD). Properties investigated cover the equation of state and transport properties (including mutual diffusion, shear and bulk viscosity, and thermal conduction). A combined Monte Carlo and molecular dynamics (MCMD) calculation for the single-component hard-sphere fluid has yielded equation of state data of extremely high precision. Combining these data with the Pade' approximants to the virial series (using the known virial coefficients through  $B_5$ ) we have obtained estimates for the sixth and seventh virial coefficients and approximants of sufficient precision to fit the MCMD data over the fluid regime, up to a density of 1/1.6 of close-packed. Study of

the shear viscosity of the hard-sphere fluid by NEMD has shown the existence of a shear-induced phase transition to a two-dimensionally ordered phase. It also shows the viscosity coefficient to decrease regularly with increasing shear rate up to the phase transition. For isotopic (mutual) diffusion, comparisons of Green-Kubo and NEMD calculations have shown the methods to agree, yielding a mutual diffusion constant roughly 13% 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. [0.5 FTE]

**National Institute for Petroleum and Energy Research (NIPER)**  
**Bartlesville, Oklahoma 74005**

**Processing and Thermodynamics** **\$177,000**

**162. Thermodynamic Characterization of Condensed-Ring Compounds**  
*B.E. Gammon*

Research continues on synthesis, purification, and measurement of thermodynamic properties of polycyclic aromatic hydrocarbons and their hydrogenation products and for similar polycyclic, organic, nitrogen compounds. These substances are important in processing of coal, oil shale, and heavy petroleum to produce liquid fuels and chemical feedstocks. Preparation of manuscripts is in progress reporting thermodynamic properties of 2,2'-dimethylbiphenyl, isoquinoline, quinoline, and 4-methylphenanthrene. Measurements are nearing completion on acridine and phenanthridine; several other compounds are purified awaiting measurements. Synthesis and purification of others are in progress. Derived Gibbs energies of formation facilitate an understanding of hydrocracking and denitrogenation. The data also form the base for improved correlations based on molecular structure. The comprehensive experimental program involves enthalpy of combustion, low-temperature adiabatic calorimetry (third-law entropy determinations), vapor pressure manometry, and Raman and infrared spectroscopy with molecular statistical mechanics. [3.0 FTE]

**Oak Ridge National Laboratory**  
**Oak Ridge, Tennessee 37831**

**Chemical Technology Division** **\$99,000**

**163. Fundamental Processes in Sorption Pumping and Transfer Operations Using Deep Beds of Sorbents**  
*C.H. Byers, J.J. Perona*

A fundamental framework for predicting the performance of deep-bed sorption systems is being developed for application to processes involving pumping, transfer, and storage of materials by sorption on deep beds of sorbents. Currently such techniques are utilized in a number of energy production and storage applications. An experimental program is in progress to determine the relative significance of heat and mass transfer, pressure drop, sorption equilibrium, and reaction kinetics. In the current phase, sorption processes at cryogenic temperatures in the molecular flow regime are controlled by mass transfer resistance. The assumptions used in an analytical solution to the problem are under experimental investigation in a recently



## OFFSITE INSTITUTIONS

## Heavy Element Chemistry

Florida State University  
Tallahassee, Florida 32306165. *Research in Actinide Chemistry*  
G.R. Choppin, Dept. of Chemistry \$95,700

This research is concerned primarily with complexes of actinide elements in aqueous solution. 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, of the kinetics of complexation, of the spectroscopic properties of complexed species using electronic (f-f) transitions and nuclear magnetic resonance and of the redox properties of the actinides. Our interest is focused on the fundamental aspects of the factors that determine the nature and extent of formation of actinide complexes. The ligand studies have potential interest in separation schemes of the actinides or in their environmental or biological behavior. It is hoped that these studies will lead to the development of useful models for the behavior of actinide ions in a variety of natural solution systems.

SRI International  
Menlo Park, California 94025166. *Chemistry of Gaseous Lower-Valent Actinide Halides*  
D.L. Hildenbrand, Physical Sciences Division \$88,400

The objective of this program 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 U-Br, Th-F, and Th-Cl systems; all of the lower-valent halides in these systems have now been generated from effusive sources, identified by mass spectrometry, and thermochemically characterized. A clear pattern of bond dissociation energies is beginning to emerge; this pattern will be useful in modeling the thermochemistry of the heavier actinide halides, which will be much more difficult to study.

University of New Mexico  
Albuquerque, New Mexico 87131167. *Development of Surface Immobilized Ligands For Actinide Separations*  
R.T. Paine, Dept. of Chemistry \$73,000

The general objectives of this program are to develop systematic synthetic methods for the attachment of extractants to solid supports and to screen the immobilized extractants as selective ion chromatography materials for the separations of metal ions present in nuclear fuel reprocessing and industrial waste solutions. Within this project fundamental investigations of steric and electronic effects which influence and modify extractant-metal ion interactions are in progress. Isolated liquid-liquid extraction complexes are studied at the molecular level by spectroscopic and x-ray crystallographic methods. The resulting molecular architecture data are used to design improved extractants and to model surface immobilized extractant-metal interactions. Extraction equilibria for several phosphonate extractants attached to polymer backbones and silica in contact with lanthanide and actinide ions are being obtained.

University of Tennessee  
Knoxville, Tennessee 37996-1200168. *Magnetic Measurements of the Transuranium Elements and Characterization of Actinides in Primary Waste Forms*  
P.G. Huray, Dept. of Physics \$100,000

A SQUID based micromagnetic susceptometer in the facilities at the Transuranium Research Laboratory is being used to measure the magnetic properties of americium, curium, berkelium, californium, and einsteinium metals and compounds. The research catalogues 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. Current work deals with the saturated moments of dhcp californium-249 metal and the degree of magnetic order attained in the limit of low temperatures and high fields. A practical result of the work is the identification of electronic configurations of transuranium elements in primary nuclear waste forms.

169. *Physical-Chemical Studies of the Transuranium Elements*  
J.R. Peterson, Dept. of Chemistry \$135,000

This program 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 for 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 con-

traction; (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 solid state (the latter as a function of temperature or pressure); (4) structural changes 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 chemistries of the transeinsteinium elements.

## Photochemical and Radiation Sciences

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

170. *Photoacoustic/Laser Spectroscopy of Halogens and Mixed Halogens For Energy Purposes*  
P. Venkateswarlu, Dept. of Physics \$100,000  
(24 mo.)

The photoacoustic spectrometer for the study of the energy level structure of the halogen molecules is being set-up. A nitrogen/dye laser system is used as the excitation source. The acoustic signals are detected with microphones. The signal processing is done by a boxcar integrator. The various components (e.g., photomultiplier and microphone detectors, amplifiers, and other optical elements) are being procured. A quartz absorption cell is also being fabricated.

### Boston University Boston, Massachusetts 02215

171. *Investigation of the Triplet States of Chlorophylls*  
R.H. Clarke, Dept. of Chemistry \$173,300  
(24 mo.)

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 and raman spectroscopy 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.

172. *Study of Intermediates From Transition Metal Excited-State Electron-Transfer Reactions*  
M.Z. Hoffman, Dept. of Chemistry \$75,000

This research is concerned with the kinetic and mechanistic behavior of intermediates that result from excited-state electron-transfer reactions involving transition metal coordination complexes, quenchers, and sacrificial electron donors in solution. These intermediates are generated by means of continuous and flash photolysis, and from the interaction of substrates with radiation-generated radicals using continuous and pulse radiolysis techniques. The emphasis of the work is currently on the modes of formation and decay of reduced viologens. Viologens form photoactive charge-transfer complexes with sacrificial electron donors; the magnitude of complexation, photoreduction, and luminescence is being studied as a function of pH and solution composition. Ion-pairing and complexation have a significant effect on the quantum yield of reduced viologen when the system is photosensitized by ruthenium(II)-polypyridyl complexes. Viologens are reduced by EDTA radicals; hydrogenation of reduced viologens is minimized, and the yield of hydrogen is maximized, upon interaction of reduced viologens with catalytic platinum in the presence of EDTA. The goal of the research is to understand the fundamental chemistry governing the generation of energy-rich charge-separated species.

173. *Formation of Fuel via Photochemical Electron Transfer*  
G. Jones, Dept. of Chemistry \$192,000  
(24 mo.)

This research involves investigation of photochemical electron transfer reactions which are of potential utility in photoformation of fuel or useful chemicals. New reagents are under development that would permit the separation of oxidation and reduction components through temporary storage of redox equivalents in stable photoproducts. Novel sulfur heterocycles capable of two-electron oxidation are of particular interest, as electron relays for experiments involving electron transfer in solution. Studies also encompass photoinduced electron transfer reactions of organic dyes which are bound to water soluble polymers. Applications of electron transfer in photochemical decomposition of hydrogen sulfide, hydrogen halide, as well as water are under consideration.

### Brandeis University Waltham, Massachusetts 02254

174. *Photochemical Reactions of Complex Molecules in Condensed Phase*  
H. Linschitz, Dept. of Chemistry \$95,000

The purpose of this project is the identification and evaluation of factors governing the efficiency of primary radical formation in photochemical redox reactions. This is a general problem in photochemical energy conversion since charge-transfer kinetic intermediates may lead either to radical products or dissipative quenching. Reaction rates and quantum yields are measured by laser flash photolysis on redox systems including particularly porphyrins or aryl ketones, with inorganic anions or water itself as donors. The major phenomena to be understood are the mechanism of the direct photoxidation of water by ketone triplets and the sharp increase in radical yield at high anion concentrations. Studies on covalently linked porphyrin-quinone sys-

tems are in progress, to determine effects of donor-acceptor distance, orientation, and dielectric medium. Spectroscopic and photochemical properties of porphyrin dimers are being studied, as models for photosynthetic reaction centers. Other research is concerned with photo-isomerization of dipyrrolyl-methenes and shifts in proton-transfer equilibria accompanying formation of rotational conformers.

### Brown University Providence, Rhode Island 02912

#### 175. *A Unified Approach to Characterization of Collisions Between Reactive Radical Pairs in Solution* R.G. Lawler, Dept. of Chemistry **\$75,000**

A project is under way to systematically characterize the reactive and unreactive encounters between simple organic and inorganic free radicals in aqueous and organic solvents by comparing the kinetics of bimolecular radical decay as measured by EPR with concurrent measurements of bimolecular contributions, especially Heisenberg spin exchange, to electron relaxation times. Radicals are generated at present primarily by pulse electron radiolysis of aqueous solutions of simple inorganic ions or organic acids and alcohols using facilities at Argonne National Laboratory. Studies are being extended to organic solvents using peroxides as radical precursors and employing EPR detected photolysis. Theoretical models are being developed both to extract data from rapidly varying magnetic resonance spectra detected by pulsed methods and to interpret the ratio of reaction to exchange probabilities in terms of molecular properties of the radicals and the medium in which they react.

### Carnegie-Mellon University Pittsburgh, Pennsylvania 15213

#### 176. *Solar Energy Conversion in Homogeneous Solution* R.M. Richman, Dept. of Chemistry **\$50,000** (9 mo.)

The goal of this project is to study the photochemistry of compounds that are likely to photodisproportionate. This mechanism has the potential for doing useful oxidations and reductions without the need for a nondissociative long-lived charge transfer excited state. Irradiation of  $\mu$ -oxo-bis((tetraphenylporphinato)-iron(III)) at  $\lambda \geq 440$  nm yields the ferryl ion, FeOTPP. Irradiation with sunlight of a cyclohexene solution results in catalytic oxidation to cyclohexene-1-one with several thousand turnovers. Inclusion of thallium (III) benzoate may yield the epoxide. Flash photolysis allows direct observation of the transient FeOTPP. Analogous photochemistry is observed with (FeTPP)<sub>2</sub>N and (FeTPP)<sub>2</sub>C. Use of charged porphyrins allows study in aqueous solution, but the quantum yield at 410 nm is still  $\sim 10^{-4}$ . Irradiation in the presence of CoTPP may yield the novel mixed-metal FeTPP-O-CoTPP. Irradiation of [Ru(NH<sub>3</sub>)<sub>5</sub>]<sub>2</sub>O<sup>4+</sup> results in substitution followed by reduction.

### Charles F. Kettering Research Laboratory Yellow Springs, Ohio 45387

#### 177. *Particulate Models of Photosynthesis* G.R. Seely, **\$67,900**

The program consists of the investigation of photophysical and photochemical properties of chlorophyll, absorbed together with other amphiphilic molecules on particles of polyethylene swollen with low molecular weight hydrocarbon diluents. When suspended in aqueous media, the particles are intended to provide a viscous medium for anchorage of the hydrophobic parts of amphiphilic molecules. In general, chlorophyll is maintained in monomeric form in the presence of amphiphiles that interact with it, such as alkylamides, or as fluorescent dimers or higher aggregates at greater concentration. Specific aspects under investigation include absorption, fluorescence, and CD spectroscopy, energy transfer among chlorophyll species, and photochemistry. With regard to the last, the behavior of particles with chlorophyll and oxidizing amphiphilic ligands is receiving particular attention.

### Clarkson College of Technology Potsdam, New York 13676

#### 178. *Photochemical Solar Energy Conversion in Surfactant Vesicles* J.H. Fendler, Dept. of Chemistry **\$155,000** (24 mo.)

Utilization of surfactant vesicles for solar energy conversion continues to be the goal of this project. The main thrust of our research has centered upon the use of vesicles and polymerized vesicles for the *in situ* generation of catalyst coated colloidal semiconductors and upon their employment in efficient solar hydrogen generation. Compartmentalization of appropriate precursors in controlled concentrations has led to the reproducible formation of small catalyst coated uniform semiconductors in the vesicles. Additionally, subsequent to band-gap excitation, undesirable electron hole back recombination has been observed to diminish in the unique microenvironments provided by the vesicles. Efficient photosensitized hydrogen generation has been demonstrated on using *in situ* generated platinum coated CdS colloidal semiconductors in vesicles. Thiophenol has been used as a sacrificial electron donor. Current research is directed toward the optimization of these and related systems.

### Clemson University Clemson, South Carolina 29631

#### 179. *Intramolecular Energy Transfer Reactions As a Method For Metal Complex Assisted Production of Hydrogen* J.D. Petersen, Dept. of Chemistry **\$135,500** (24 mo.)

The current research effort 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. Major emphasis has been on bridging ligands that will chelate both metal centers such as 2,2'-bipyrimidine and 2,2'-biimidazole, and form short, highly-conjugated links

[Ru(bpym)Cl<sub>2</sub>]<sub>x</sub>(bpym)<sub>y</sub>, which is black in color and has two potential derivative sites on each metal center.

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

**180. Laser Enhanced Chemical Reaction Studies**  
G.W. Flynn, Dept. of Chemistry \$90,000

This project is aimed at the 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 being 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. Infrared fluorescence is being used to probe the broad spectral distribution of vibrationally and rotationally hot CO, CO<sub>2</sub>, and CH<sub>3</sub>F molecules produced in these atom-molecule encounters. An infrared laser diode is also employed to monitor, with a resolution of milliwavenumbers, the precise vibrational and rotational states excited during such collisions. Laser induced visible and U.V. fluorescence methods are being used to identify the species, and to measure the distribution of final states formed as a result of chemical reaction.

**Dartmouth College**  
Hanover, New Hampshire 03755

**181. Photoexcited Charge Pair Escape and Recombination**  
C.L. Braun, Dept. of Chemistry \$81,500  
(24 mo.)

The escape and recombination of charge pairs produced by photoexcitation of organic molecules is being studied. The recombination of geminate charge pairs formed by the photoionization of solute molecules in low dielectric constant solvents is found to occur in picoseconds. This process is being studied by pump-probe conductivity techniques. Picosecond absorption measurements of the recombination kinetics are planned. The data are being compared with a detailed theory of the diffusive recombination of geminate charge pairs. 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 being 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 being used to test mechanistic ideas.

**Louisiana State University**  
Baton Rouge, Louisiana 70803-0301

**182. Theoretical Studies of Electron and Proton Transfer Processes in Fluids**  
N.R. Kestner, Dept. of Chemistry \$60,000

This research program is designed to study electron and proton transfer processes in fluids, especially those which could be important in energy conversion. General theoretical studies are

probing the role of temperature, pressure, and solvent effects on electron transfer rates. Our special attention is directed to such effects for reactions in the abnormal, or highly exothermic regions. Related work is exploring structure-activity relations, which are important in the related proton transfer processes. The general theories are being applied to specific reactions. In this regard, we are determining very accurate water-water interactions and other intermolecular potentials, exploring in detail the role of basis set errors. These are being used to obtain accurate interaction energies between electron transfer species such as Fe(II) and Fe(III) in aqueous solutions. Other studies are directed at predicting electron transfer rates in glasses, and highly viscous media.

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

**183. Photochemical Energy Storage: Studies of Inorganic Photoassistance Agents**  
M.S. Wrighton, Dept. of Chemistry \$270,000

Light-driven, energy-storing chemical reactions are the object of study in this research program. Emphasis is on the use of semiconductor electrodes as the photoassistance agents for redox reactions such as the oxidation and reduction of H<sub>2</sub>O. 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 program. Semiconductor materials under study in this connection include WS<sub>2</sub>, InP, GaAs, Si, CdX (X=S, Se, Te), and amorphous hydrogenated Si. Another aspect of the program is chemical derivatization of the semiconductor surface for the purpose of improving 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<sub>2</sub>O reduction have received most attention. Exploratory studies to find unique interactions of redox reagents with semiconductor electrode surfaces, such as I<sub>3</sub><sup>-</sup>/I<sup>-</sup> with n-WS<sub>2</sub>, are in progress. Such unique interactions are likely to lead to high efficiency for energy conversion and specific redox processes.

**Mount Holyoke College**  
South Hadley, Massachusetts 01075

**184. The Study of the Photochemistry of Organic Dyes at Semiconductor Electrodes Using Total Internal Reflection Techniques**  
M.T. Spitler, Dept. of Chemistry \$65,399

The photochemistry of organic dyes adsorbed at semiconductor surfaces is being studied through a combination of photoelectrochemical and total internal reflection techniques. The utilization of an attenuated total reflection method enables an *in situ* determination of the quantum efficiency of current producing photoreactions. The photochemistry of dyes at ZnO, TiO<sub>2</sub>, and SrTiO<sub>3</sub> single crystal surfaces is being investigated using dyes that show significant triplet character or tendency to form aggregates. Selected photoreactions will also be studied at surfaces chemically modified in differing regions of donor and acceptor to serve as a model for catalytic photoreactions at powders.

## National Bureau of Standards Washington, District of Columbia 20234

### 185. *Support of Critical Data Compilations* D.R. Lide, Jr., Office of Standard Reference Data **\$200,000**

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 which allow prediction of unmeasured properties. Reviews are in press on high-temperature vaporization of alkali metal oxides, water solubility of polynuclear aromatic compounds, electrochemical equilibria in carbon-oxygen systems, and other topics.

### 186. *Pulse Radiolytic Studies of Inter- and Intramolecular Electron Transfer Processes* P. Neta, Center for Chemical Physics **\$135,000**

Studies of both intermolecular and intramolecular 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. Quantitative results are obtained, detailing the effects on the rates of intramolecular electron transfer of the charge distribution within the molecule, electron affinities of substituents, steric effects, and other structural parameters. Intramolecular electron transfer reactions within metalloporphyrins are also studied, because of the importance of these molecules in photosynthesis, and because they allow a detailed analysis of the effect of driving force and other parameters on the rates of these processes. The mechanism and thermodynamics of intermolecular electron transfer reactions are studied, using measurements of rate and equilibrium constants as a function of temperature to obtain quantitative information about activation energies, enthalpy, and entropy changes associated with these processes. Comparison of values of liquid and gas phase systems will permit a more quantitative understanding of solvation effects in electron transfer processes. Electron transfer reactions of metalloporphyrins and their anion- and cation- radicals with a variety of other chemical systems and especially with certain metal catalysts are being studied as models for understanding artificial photosynthesis and other photochemical processes involving porphyrins.

## Ohio State University Columbus, Ohio 43210

### 187. *Pulse Radiolysis Studies of Fast Reactions in Molecular Systems* L.M. Dorfman, Dept. of Chemistry **\$22,000**

The broad objective of this research project is to come to an understanding of the rates and mechanisms of chemical reac-

tions induced by ionizing radiation. At the same time, the information generated about the reactive intermediates (free radicals, molecular cations, and anions) is of interest in other areas of chemistry as well. Reaction is initiated by a high energy electron pulse of submicrosecond duration, and the reactive intermediates are directly observed by fast optical absorption measurement (time resolution 5 nanoseconds). These observations also provide the optical spectra of the reactive transients. Systems presently under study are organic molecular cations and anions in solution, where the ions, important in radiation-induced reactions, also play a key role in cationic polymerization. Since the reactions are initiated by high energy electrons, the results obtained relate directly to radiation chemistry.

### 188. *Kinetics of Fast Reactions of Excited Species* R.F. Firestone, Dept. of Chemistry **\$82,000** (14 mo.)

The project objective is identification of mechanisms for growth and decay of excited rare gas atoms and excimers in the presence and absence of foreign quenching agents, using pulse radiolysis methods. Identities of excited atomic precursors of bound excimer states are sought by modeling of a multi-stage reversible collisional relaxation mechanism for rovibrationally excited excimer molecules, in conformity with temporal behavior of excited atoms and rovibrationally relaxed excimers. Monitoring of excited species is done by emission spectrometry and tunable cw laser spectrophotometry. Kinetic parameters of selected 1s-2p state pairs are to be obtained by cw pumping, coupled with absorption measurements at low power densities, and at power densities sufficiently great to induce bleaching of the transition.

## Oregon Graduate Center Beaverton, Oregon 97006

### 189. *Fundamental Studies in Charge Separation At Interfaces in Relation to Water Photolysis* J.K. Hurst, Dept. of Chemical, Biological & Environmental Sciences **\$90,000** (16 mo.)

This research is directed toward improving our conceptual understanding of the influence of microphase separation and compartmentation upon photostimulated redox processes. Three distinct activities are encompassed by these studies: (1) examination of mechanisms of transmembrane redox bilayer membranes; (2) development of inorganic two-photon excitation schemes for transmembrane charge separation; and (3) development of reversed micellar assemblies for water photolysis. Redox systems under study which exhibit net electron exchange across bilayers include lecithin-bound amphiphilic 4-alkylpyridinepentaammineruthenium<sup>2+/3+</sup> ions and dihexadecylphosphate-bound alkylviologen<sup>+ /2+</sup> ions. Studies in two-photon excitation are based upon photoreduction of cupric ion to cuprous  $\pi$ -complexes which are capable of long-range photoinitiated electron transfer to oxidant sites. In reversed micelles, the relationship between O<sub>2</sub> and H<sub>2</sub> yields, and the topographic organization of Zn(II) porphyrin sensitizers, viologen charge relays, and colloidal RuO<sub>2</sub> and Pt sols is being explored. For all photoinitiated systems, pulsed laser spectrophotometry is being used to probe reaction dynamics.

**Pennsylvania State University**  
**University Park, Pennsylvania 16802****190. The Free-Radical and Ion Chemistry of Volatile Silanes, Germanes, and Phosphines**  
*F.W. Lampe, Dept. of Chemistry* **\$104,000**

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 knowledge and 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  $\text{SiH}_4\text{-HCl}$  and  $\text{SiH}_4\text{-GeH}_4$  mixtures,  $\text{CH}_3\text{SiH}_3$ , the vacuum-ultraviolet photochemistry of  $\text{GeH}_4$  and  $\text{SiH}_4\text{-GeH}_4\text{-NO}$  mixtures, as well as the ion chemistry of  $\text{SiH}_4\text{-CH}_3\text{Cl}$ ,  $\text{SiH}_4\text{-CH}_2\text{Cl}_2$ ,  $\text{SiH}_4\text{-CHCl}_3$ ,  $\text{SiH}_4\text{-CCl}_4$ , and  $\text{CH}_4\text{-HCN}$  mixtures.

**Princeton University**  
**Princeton, New Jersey 08544****191. Photoelectrochemistry With Chemically Modified Electrodes**  
*T.G. Spiro, Dept. of Chemistry* **\$85,000**

The electrochemistry and photoelectrochemistry of metalloporphyrin electrode films is being explored, with a view toward catalyzing useful energy storage reactions, including the splitting of water to  $\text{H}_2\text{O}_2$ . Stable metalloprotoporphyrin films have been prepared via electroinitiated polymerization of the vinyl side-chains, and other porphyrin polymerization schemes are being explored. Cobalt porphyrins are being applied to the catalysis of  $\text{H}_2$  production from water. The kinetics of the catalysis have been investigated in homogeneous solution using electrochemical techniques, and cobalt porphyrin electrode films have been developed, which are capable of sustained  $\text{H}_2$  production, and their characteristics are being explored. Iron, chromium, and manganese porphyrins are being explored in oxidative chemistry, with the eventual aim of catalyzing water oxidation.

**Purdue University**  
**West Lafayette, Indiana 47907****192. Study of the Motion of Electrons in Non Polar Classical Liquids**  
*G. Ascarelli, Dept. of Physics* **\$69,000**

In our study of the properties of electrons injected into a liquid, we have calculated the expected drift mobility in liquid Ar assuming that the primary scattering mechanism is due to thermal phonons. In this case, the deformation potential that appears in the expression for acoustic phonon scattering is  $\Xi = -n(dV_0/dn)$ . To take into account the fact that we are considering an electron moving in a liquid, rather than a crystal, we considered the density fluctuations in a volume whose dimensions are equal to the thermal wavelength of the electron. These fluctuations assure that the mobility remains finite even when  $dV_0/dn = 0$ . Their effect is also to increase the mobility near the critical point by decreasing the phonon amplitude inside of a

density fluctuation where the electron is located. The resulting mobility near the critical point, assuming  $m^* = m_0$  is  $1900\text{cm}^2/\text{Vs}$  decreasing to  $500\text{cm}^2/\text{Vs}$  when the density is  $1.5 \times 10^{22}\text{cm}^{-3}$ . A maximum mobility of  $5000\text{cm}^2/\text{Vs}$  is predicted where  $dV_0/dn = 0$  and a mobility equal to  $50\text{cm}^2/\text{Vs}$  is predicted at the critical point. Our preliminary Hall mobility measurement in Ar at a density  $2 \times 10^{22}\text{cm}^{-3}$  is  $1600\text{cm}^2/\text{Vs}$ . From it, a drift mobility of  $1355\text{cm}^2/\text{Vs}$  is calculated. This value is in excellent agreement with the phonon scattering calculation ( $1340\text{cm}^2/\text{Vs}$ ) alluded to above.

**Stanford University**  
**Stanford, California 94305****193. Energy Transfer Processes in Solar Energy Conversion**  
*M.D. Fayer, Dept. of Chemistry* **\$110,000**

This project is examining energy transport processes in nontraditional systems, using picosecond and other optical techniques and statistical mechanical theoretical methods. There are a wide variety of situations in both natural and man-made systems which 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 to study energy transport among dye molecules attached to long hydrocarbon chains organized in micelle solution, and to examine energy transport in chromophore containing polymers. These clustered chromophore systems permit extremely high local chromophore concentrations (and therefore efficient energy transport), without the normal energy quenching associated with conventional concentrated dye solutions. In addition, we are studying electron transport in disordered systems. Using picosecond lasers, electron transport between organic molecules is examined on a timescale fast enough to show the dynamical details important in natural and laboratory chemical electron transfer reactions. Electron transport in amorphous silicon is under investigation with transient grating techniques.

**194. Fundamental Electron Transfer Processes At the Semiconductor/Liquid Interface**  
*N.S. Lewis, Dept. of Chemistry* **\$150,000**  
**(24 mo.)**

Variations in fundamental electron transfer parameters at the semiconductor/liquid interface are studied with systematic changes in bulk semiconductor composition in the  $\text{GaAs}_{1-x}\text{Px}$  and  $\text{Al}_{1-x}\text{Ga}_x\text{As}$  series of alloys. We have obtained single crystal, epitaxially grown, n-type samples of representative members of these series, and have investigated changes in electrode properties in both aqueous and nonaqueous solvents. In aqueous selenide-containing solutions, we observe stable photoanode behavior for all members of the series, and observe high spectral response characteristics for all materials. Similar behavior is found in nonaqueous solvents, and in both solvent systems the photoanode properties seem more strongly correlated to the bulk semiconductor band gap than to the actual bulk or surface composition of the electrode. More detailed measurements on the variation of properties in this system are in progress.

**Temple University**  
Philadelphia, Pennsylvania 19122

- 195. *Dynamic Aspects of the Dye-Sensitized Photo-conductivity of Semiconductors***  
A.M.P. Goncalves, Dept. of Chemistry **\$80,000**  
(14 mo.)

The objective of this program is to probe the dynamics of the elementary processes (injection, recombination, and escape) which determine the efficiency of dye-sensitized semiconductor/electrolyte solar cells. The general experimental approach relies primarily on the use of subnanosecond time-resolved spectroscopic techniques: fluorescence and transient absorption or gain. The fluorescence lifetimes of several dyes adsorbed on semiconductors and insulators at high surface coverage (measured with streak camera detection) are on the order of 50 picoseconds, as much as 30 times shorter than in solution. The fact that a similar lifetime reduction occurs for each dye, both on semiconductor and insulator surfaces, suggests that energy transfer quenching is primarily responsible for the short lifetimes. This is confirmed by fluorescence quantum yield measurements as a function of surface coverage: in the limit of very low surface coverage, the quantum yield approaches the solution value on an insulator and a much smaller value on a semiconductor. These experiments indicate that injection occurs in a time on the order of 150 ps. More recent measurement of the fluorescence lifetimes at very low surface coverage (using a time-correlated single photon counting technique) have provided a much more reliable direct measurement of the injection time: 400 ps.

**University of Alabama**  
Tuscaloosa, Alabama 35486

- 196. *ELDOR Investigations of Radiation Processes***  
L.D. Kispert, Dept. of Chemistry **\$66,700**

The objective of this research is to determine how a 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, and electron-electron double resonance techniques are being used to identify the molecular fragments formed and to detect the energy transfer processes that occur. In particular, selected sugar, polyalcohol, carboxylic acid, and acetamide crystals are being studied to determine the effect of hydrogen bonding on radical stability and reaction mechanisms as a function of temperature in crystals containing (1) varying crystallographic forms, (2) rotational disorder, and (3) impurities. 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, photoexcited triplet state lifetimes have been measured, and halogenated organic anions have been detected.

**University of Arizona**  
Tucson, Arizona 85721

- 197. *Mechanisms of Photochemical Energy Conversion By Chlorophyll***  
G. Tollin, Dept. of Biochemistry **\$160,600**  
(24 mo.)

The goals of this project are to elucidate the detailed mechanisms involved in light-induced one-electron transfer reactions involving chlorophyll (and related compounds) and electron donors and acceptors, and 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 which 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. Current work involves the use of laser flash photolysis to monitor excited state and radical dynamics in lipid bilayer vesicle systems.

**University of California/Irvine**  
Irvine, California 92717

- 198. *Research in Chemical Kinetics***  
F.S. Rowland, Dept. of Chemistry **\$180,000**

This research project is directed toward the understanding of the rates and mechanisms of chemical reactions, including some of interest to atmospheric chemistry. The reactions of thermalized  $^{18}\text{F}$  and  $^{38}\text{Cl}$  atoms with gaseous  $(\text{CH}_2=\text{CHCH}_2)\text{M}$  compounds are being studied for  $\text{M}=\text{Sn, Ge, Si, C}$  to determine the extent of restricted intramolecular energy flow ("non-RRKM") in such systems. Reactions of halogen atoms with haloolefins ( $\text{X} + \text{CH}_2=\text{CHY}$ ;  $\text{X}=\text{F, Cl}$ ;  $\text{Y}=\text{F, Cl, Br}$ ) are furnishing rate information about radical lifetimes, and mechanistic information such as selectivity and isomerization. The temperature dependence of  $^{38}\text{Cl}$  reactions with olefins is being studied over the 240-360 K temperature range. The mechanism of the direct gas-phase photolysis of  $^{14}\text{CS}_2$  is being investigated with and without  $\text{O}_2$  present. The rates and mechanisms of hydrolysis in aqueous solution are being measured for gases occurring in the atmosphere, including  $\text{OCS}$ ,  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{Br}$ . The gas phase photolyses of  $\text{PH}_3$  and  $\text{P}_2\text{H}_4$  and the co-photolysis of  $\text{PH}_3$  and  $\text{NH}_3$  are being investigated. The possibility of hot Cl abstraction by energetic  $^{38}\text{Cl}$  atoms is being tested.

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

- 199. *Time-Resolved Laser Studies On the Energy Transfer and the Configurational Changes in Bacteriorhodopsin***  
M.A. El-Sayed, Dept. of Chemistry **\$100,000**

Bacteriorhodopsin (BR) is another photosynthetic system besides chlorophyll. While chlorophyll uses electron pump, BR uses 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 in order to record the spectra of the different transients formed following the initial photosynthetic absorption process. Questions such as: (1) does energy

migration take place to specific sites prior to photochemistry; (2) does isomerization of retinal take place on the picosecond time scale; and (3) how does the Schiff base lose its proton during the photochemical cycle, are among the questions we are attempting to answer. Very recently, we started using time-resolved optical spectroscopy of the protein and the retinal systems, to identify the nature of the coupling between these two systems which is undoubtedly responsible for the proton pumping required for photosynthesis in bacteriorhodopsin.

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

**200. Energy Transformations in Transition Metal Complexes**  
*R.J. Watts, Dept. of Chemistry* **\$89,300**

The projects in this program are intended to explore basic photochemical and photophysical phenomena in transition metal complexes. Five 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) photochemistry and photophysics of organometallic sandwich complexes. Techniques being applied in these projects include time-resolved emission spectroscopy, laser-induced transient and excited state absorption spectroscopy, and  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectroscopy. Laser double resonance techniques are presently being developed for the purpose of characterizing electronic relaxation between excited states of metal complexes. Synthesis and characterizations of complexes containing metal-carbon bonds are being carried out in order to facilitate the projects in area (1) above. The emission spectroscopy and photoinduced electron transfer reactions of several of these complexes are presently under investigation.

**University of Colorado**  
**Boulder, Colorado 80309**

**201. Chemical Probes of Charge Transfer At Semiconductor/Liquid Junctions**  
*C.A. Koval, Dept. of Chemistry* **\$75,000**

The surface energetics for p- and n-InP/ $\text{CH}_3\text{CN}$  and p- and n- $\text{WSe}_2$ / $\text{CH}_3\text{CN}$  interfaces are being carefully examined with capacitance measurements. This information is used to interpret the kinetic aspects of voltammograms obtained at these electrodes for a series of metallocene $^{+0}$  redox couples. Complexes with the general formula  $\text{Cr(III)(NH}_3)_5(\text{RCO}_2)^{2+}$  are being examined for use in experiments to detect non-thermalized, photogenerated electrons (hot carriers). Metallocenes with charged substituents ( $-\text{NR}_3^+$ ,  $-\text{COO}^-$ ) are used to investigate diffuse-layer effects at semiconductor/liquid junctions. These experiments are designed to delineate fundamental kinetic aspects of charge transfer at semiconductor/solution interfaces, with the ultimate goal of improving efficiencies and lowering costs for devices based on photoelectrochemical cells.

**University of Florida**  
**Gainesville, Florida 32611**

**202. Radiation Chemistry of Hydrocarbon and Alkyl Halide Systems**  
*R.J. Hanrahan, Dept. of Chemistry* **\$71,000**

Current work is directed towards understanding the mechanism of product formation in the gamma and pulsed electron radiolysis of simple chemical systems. Studies of the radiolysis of hydrogen-carbon monoxide mixtures on alumina surfaces include measurement of both hydrocarbon and oxygen-containing products; certain yields are increased by 100 times or more in comparison to the gas phase. The radiolytic oxidation of propane shows many similarities to auto-oxidation in products and reaction pathways; computer modeling of the reaction scheme accounts for the oxygen pressure dependence of product yields. Measurements are being made on the rates of attack of OH radicals on hydrocarbon and halocarbon gases, using the pulse radiolysis method. Comparison of results at high and low water concentration yields data on the rates of OH + radical combination reactions in these systems. Photolysis of methyl iodide-perfluoromethyl iodide mixtures forms several products, including: (1) methane and perfluoromethane; (2) ethane and perfluoroethane; and (3) several mixed products such as trifluoromethane, difluoroethylene, and trifluoroethane, along with HI and HF.

**University of Houston**  
**Houston, Texas 77004**

**203. Charge Separation in Photoredox Reactions**  
*L. Kevan, Dept. of Chemistry* **\$90,000**

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 (TMB) has been photoionized to produce the cation radical in liquid and frozen micellar solutions of anionic, cationic, and nonionic surfactants, and in liquid and frozen synthetic, anionic, and cationic vesicle solutions. The cation is observed by optical absorption, electron spin resonance, and electron spin echo spectrometry. Cation-water interactions, detected by electron spin echo modulation analysis, indicate that the photoproduct cation is located asymmetrically within both the micellar and vesicular structures, and generally correlates with photoionization efficiency. Micelle surface modification by added salts and varying counterions has led to some control of photoionization efficiency. The decay kinetics of photo-produced cations in micelles have been found to be characterized by time dependent rate constants.

**University of Massachusetts**  
**Boston, Massachusetts 02125**

**204. Investigation of the Structure of Photosynthetic Reaction Centers**  
*H. van Willigen, Dept. of Chemistry* **\$68,500**

The structure of photosynthetic reaction centers and model systems is studied with the aid of magnetic resonance techniques and optical spectroscopy. Research has focused on the applica-

tion of Electron Spin Resonance (ESR) in the study of photo-excited triplets of a series of porphyrins. The spectroscopic data give information on the structure of aggregates of these systems and give an insight into their photophysical and photochemical properties. The study is concerned as well with the application of Electron Nuclear Double Resonance (ENDOR) in the study of the electron spin distribution in the photo-excited triplets. The method has been used to measure hyperfine interactions in the photo-excited triplets of the primary donor in reaction center preparations of photosynthetic bacteria.

**University of Minnesota**  
Minneapolis, Minnesota 55455

**205. *The Contribution of Electronically Excited States to the Radiation Chemistry of Organic Systems***  
*S. Lipsky, Dept. of Chemistry* **\$100,000**

A general study is being made of those photophysical properties of organic molecules that have relevance in determining their radiation-chemical behavior. Projects currently in progress include: (1) a study of the dependence on scavenger concentration of the efficiency of quenching geminate-ion recombination fluorescence of saturated hydrocarbon liquids, in order to characterize the distribution of electron-positive ion separation distances; (2) a study of the dependence on photon energy of the probability of photoionization and of the average range of the electron ejected from aromatic solutes in non-polar fluids, via comparison with theory of the effect of an electric field to reduce the geminate-ion recombination fluorescence; (3) a study of the effect of perfluorocarbons to alter the distribution function of electron-positive ion separation distances by interaction with epithermal electrons as manifested by an altered electric field dependence of photocurrent.

**University of Nebraska**  
Lincoln, Nebraska 68588-0304

**206. *Electrochemical and Optical Studies of Model Photosynthetic Systems***  
*T.M. Cotton, Dept. of Chemistry* **\$75,000**

A combination of electrochemical and resonance Raman techniques, supplemented by ultraviolet-visible spectroscopy, is being used to characterize some important properties of the pigments of the bacterial photosynthetic reaction center. Characterization includes determination of the redox states of the various components during the initial photoact as well as the identity and spectral character of the neutral and charged species involved. Much of the present knowledge of the primary photoact in photosynthesis is based on *in vitro* measurements or on *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. Attempts are under way to incorporate bacteriochlorophyll, bacteriopheophytin, and quinones from reaction centers into monolayer arrays. In these designed monolayer constructions the orientation, spacing, and identity of the included components are under a high degree of control. 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.

**207. *Energetics of the Formation and Reactions of Gaseous Ions***  
*G.G. Meisels, Dept. of Chemistry* **\$85,000**

Two areas are addressed in this research program. One area uses threshold photoelectron - coincident photoion mass spectrometry to study ions whose internal energies are known within 0.025 eV. The other area derives the spatial distribution of ionization by 100 to 1000 eV electrons from ion residence times in the chemical ionization source of a mass spectrometer. In the first area, the energetics of the formation, isomerization, and fragmentation of gaseous cations are measured. Anisole and dimethylether show stable molecular ions several eV above fragmentation onset, and thus do not, at all energies, behave in accordance with statistical theories. In the second area, linear ionization rates are measured as a function of beam penetration into the ion source; they increase briefly from the point of beam entry and then decrease smoothly. Ranges derived from them for methane, nitrogen, and the rare gases lie between those measured by bulk techniques and the probable electron path length. The coaxial geometry and preferential detection of ions formed along the beam axis permit evaluation of both longitudinal and radial distributions of ion formation.

**208. *High Energy Halogen Reactions Activated By Nuclear Transformations***  
*E.P. Rack, Dept. of Chemistry* **\$71,600**

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 ( $^{\text{S}}\text{H}^2$ ) at the chiral centers of chiral 2-halopropionyl halides is currently studied. Practical applications of recoil atom chemistry to activation analysis or 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 biological molecules are being carried out.

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

**209. *Energy Conversion Processes Based On Molecular Excited States***  
*T.J. Meyer, Dept. of Chemistry* **\$105,000**

This research effort is based on the study and exploitation of excited states of transition metal complexes. A particularly important goal is the design and characterization of new classes of photosensitizers, and their application to solar energy related problems. In technical detail the work involves the measurement of the photochemical and photophysical properties of excited states, the application of theory to such processes, synthesis of new types of potential photosensitizers, the preparations and properties of metallopolymers containing metal complex chromophores, the study of electron and energy transfer processes

of the photosensitizers in solutions and polymeric films, and possible applications of these materials in photochemical and photoelectrochemical energy conversion processes.

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

**210. Oligomer and Mixed-Metal Compounds, Potential Multielectron Transfer Catalysts**  
D.P. Rillema, Dept. of Chemistry \$60,100

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 multi-metal complexes capable of "simultaneous" multielectron transfer. The characterizations include: (1) isomer separation of metal complexes containing assymmetric 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.

**University of Puerto Rico**  
Mayaguez, Puerto Rico 00708

**211. Photoelectrochemistry of New Phenothiazine Dye Derivatives**  
F.A. Souto, Dept. of Chemistry \$125,000  
(24 mo.)

This project has been designed to explore the potential of amphiphilic derivatives of thionine for the study of photochemical and other energy conversion systems in aqueous solution. Emphasis is placed on the synthesis and identification of lipophilic, amphiphilic, and hydrophilic derivatives of thionine. These dyes have a great potential to alleviate the problems that prevent efficient electron-transfer quenching from taking place in concentrated solutions of photoredox couples. Our approach to this fundamental aspect of photoelectrochemistry consists in the study of the photophysical, photochemical, and electrochemical processes involved in the electron-transfer quenching of excited amphiphilic organic dyes solubilized within surfactant micellar assemblies. The initial results on the aggregation of thionine and its disulfonated derivatives indicate that their kinetic properties and thermodynamic characteristics are highly dependent on their ionic character and distribution of polar groups on the periphery of the phenothiazine nucleus. Therefore, a considerable experimental effort has been devoted to the unambiguous identification of each derivative. High frequency (470 MHz)  $^1\text{H}$  NMR spectra for each derivative in monomeric form has been the key to the solution of this activity. The photochemical and electrochemical characterization of these derivatives is in progress at this time. The indication is that 4,6-disulfonated thionine is the preferred isomer for its kinetic characteristics.

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

**212. Applications of Photo-Induced Electron Transfer and Hydrogen Abstraction Processes to Chemical and Electrochemical Conversion Processes**  
D.G. Whitten, Dept. of Chemistry \$190,000  
(24 mo.)

This research program involves studies of photochemical redox reactions occurring via electron transfer and hydrogen atom abstraction processes initiated by excitation of chromophores absorbing visible and near ultraviolet light. A part of the project involves direct study of photochemical reactions and external factors that can modify them. In addition, photoelectrochemical processes based on them are being investigated. Our studies of direct photochemical reactions have recently focused on photoredox reactions of certain indigo dyes. These dyes undergo net photoreduction processes with a variety of electron donors by, in some cases, a multiplicity of mechanisms. Among the most interesting mechanisms is a net hydride ion transfer that occurs via a sequence of electron, proton, and second electron transfer, all within the initially formed encounter complex. We are also investigating the effect of inclusion complex formation on reactivity using various amylose derivatives as selective hosts for a variety of reactive substrates. The photoelectrochemical studies are currently focusing on hydrogen atom abstraction reactions from alcohols occurring with substrates excited by visible light.

**University of Tennessee**  
Knoxville, Tennessee 37996-1600

**213. Studies of Radiation-Produced Radicals and Radical Ions**  
T.F. Williams, Dept. of Chemistry \$96,000

The basic objective of this project is to characterize important free radical and radical ion intermediates generated by irradiation of molecular systems. Current emphasis is being placed on the radical ions produced in the primary chemical processes resulting from the absorption of high energy radiation. Novel radical ions derived from typical saturated molecules are being generated and stabilized in suitable solid matrices, examples being fluorocarbon radical anions in hydrocarbon matrices and the radical cations of alkanes, ethers, and organometals of Group IVB alkyls in fluorocarbon matrices. Electron spin resonance (ESR) spectroscopy is used to identify these paramagnetic species. Measurements of hyperfine coupling constants, including those of  $^{13}\text{C}$ -labeled radicals, provide information about geometrical structure and spin density distribution. The chemical rearrangement of positive ions is also being investigated. Studies are also underway on the generation and characterization of organometallic radicals and radical ions in systems which are relevant to catalysis and solar energy conversion.

**University of Texas**  
Austin, Texas 78712

**214. Organic Redox Phototransformations at Chemically Modified Surfaces**  
M.A. Fox, Dept. of Chemistry \$70,000

Exploratory and mechanistic studies of new chemical transformations of organic molecules at native and chemically modified

surfaces represent the goal of this research program. New electrode materials are being prepared by adsorption, covalent attachment, polymerization, and mulling with electroactive or light-sensitive materials; and physical studies of the properties of these materials are being 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. Several spectroscopic techniques are being used to evaluate intermediates and surface states: (1) Fourier transform infrared spectroscopy; (2) Resonance Raman spectroscopy; (3) laser-induced flash coulometric measurements; (4) photochemically induced magnetic resonance; (5) picosecond laser spectroscopy; (6) rotating ring disc electrochemical techniques; and (7) ESCA and Auger spectroscopy. New metal non-oxides and p-type semiconductors are also being investigated, and the search for new reactions on these novel materials is continuing.

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

**215. Reaction Studies of Hot Silicon and Germanium Radicals**  
*P.P. Gaspar, Dept. of Chemistry* **\$93,000**

The goal of this research project is to discover: (1) what are the reactions of high energy Si and Ge atoms; (2) how do the reactions take place; and (3) how are the reaction pathways influenced by the energy and electronic state of the free atoms, and of the reactive intermediates that they produce. Silicon and germanium atoms are formed at high energies by nuclear transformations such as  $^{31}\text{P}_{(n,p)}^{31}\text{Si}$  and  $^{76}\text{Ge}_{(n,2n)}^{75}\text{Ge}$ , and at low energies by thermal evaporation. Intermediates such as  $\text{SiH}_2$  and  $\text{GeMe}_2$  are generated by pyrolysis and photolysis. In the past year the silylsilylene-to-disilene rearrangement has been demonstrated in a hot-atom experiment. Unsubstituted  $\text{H}_3\text{Si}-^{31}\text{Si}-\text{H}$  from reaction of recoiling silicon atoms with silane has been shown to rearrange to  $\text{H}_2\text{Si}=\text{SiH}_2$ , which was trapped with butadiene. The mechanism of addition of silylenes to 1,3-dienes has been established as consisting of a concerted 1,2-addition followed by competing Si-C and C-C bond cleavages in the opening of the silirane ring. Rate measurements on the reactions of two silylenes, Me-Si-Ph and  $\text{Me}_2\text{Si}$ , have been carried out by laser flash photolysis.

**Wayne State University**  
Detroit, Michigan 48202

**216. Dynamics of Charge-Transfer Excited States Relevant to Photochemical Energy Conversion**  
*E.C. Lim, Dept. of Chemistry* **\$76,800**

The purpose of this research is to gain fundamental understanding of radiationless transitions in exciplexes and charge-transfer complexes, which are pertinent to photochemical energy conversion. Both the steady-state and time-resolved measurements of fluorescence and triplet formation are employed to study factors which influence various nonradiative decay channels in condensed phase. The results indicate that the dominant nonradiative decay channel of these species at moderately high temperatures (room temperature and above) may be internal conversion to the ground state. They also suggest that there is a propensity rule for singlet-triplet intersystem crossing in charge-transfer

complexes. Thus, singlet-triplet intersystem crossing from a charge-transfer singlet state appears to be efficient only when a locally excited triplet state of a component molecule (donor or acceptor) lies below the charge-transfer singlet state, consistent with vanishingly small spin-orbit coupling between charge-transfer states.

## Chemical Physics

**Aerodyne Research, Inc.**  
Billerica, Massachusetts 01821

**217. A Study of CH Reactions Relevant to Combustion/Gasification Processes**  
*J.A. Silver, G.W. Stewart, Center for Chemical and Environmental Physics* **\$88,200**

Little is known about the reactions of monovalent carbon radicals known as carbynes, and in particular, those of CH radicals. Yet they play an important role in the chemistry of combustion and gasification processes, including the formation of  $\text{NO}_x$  via the prompt-NO mechanism. They also appear to serve well as a testbed for studying the mechanistic behavior of four-center reactions, and appear to exhibit both abstraction and addition at different temperatures. We are involved in a project of basic research in which both rate constants and product distributions are determined from reactions of CH with other small molecules found in combustion streams. These studies are performed on a high temperature fast flow reactor, capable of operating between room temperature and 1500 K. The goal of this project is to improve our fundamental understanding of the chemistry of carbynes.

**Brown University**  
Providence, Rhode Island 02912

**218. Interactions of Molecules With Surfaces**  
*E.F. Greene, Dept. of Chemistry* **\$74,200**

The rate of desorption of Cs, K, Na, and Li atoms from the (100) and (111) surfaces of silicon is followed by surface ionization. The rates are markedly lower from surfaces stable in the temperature range 800-950K than they are from metastable ones supercooled below surface phase transitions. These are the well-known one for (111) at  $1120 \pm 40\text{K}$ , and one for (100) at  $980 \pm 20\text{K}$ . On the metastable surfaces the desorption is first order and the atoms appear to be highly mobile. On the stable surface where the desorption is mixed, first and second order the atoms are also highly mobile but concentrated at steps between terraces from which most of the desorption occurs. In a different experiment molecules of tetramethyldioxetane are given kinetic energy by being seeded into nozzle beams of hydrogen. This kinetic energy is converted by a single collision with a surface into internal energy of the molecules, which then can decompose and emit light. The amount of light varies with the kinetic energy, the temperature of nozzle, and the nature of the surface. This experiment offers an effective method of activating the decomposition of gaseous molecules.

**California Institute of Technology**  
**Pasadena, California 91125**

**219. High Resolution Infrared Spectroscopy: Dynamics of Vibrationally Excited States**  
*K.C. Janda, Dept. of Chemistry* **\$68,000**

Molecular beam laser photodissociation spectroscopy is used to characterize intramolecular energy redistribution in excited vibrational states of molecules. Van der Waals molecules are used as prototypes for this effect because deposition of one infrared photon is enough to break a bond. The goal is to have a description of the internal molecular energy transfer in microscopic detail. It appears that vibrational predissociation of triatomic molecules is well described by Fermi's golden rule perturbation theory. This theory predicts that a HeI<sub>2</sub> molecule would have short-lived vibrationally excited states, 10<sup>-10</sup> sec., while the NeCl<sub>2</sub> molecule would have long-lived vibrationally excited states, greater than 10<sup>-5</sup> sec. This dramatic dependence of predissociation lifetime on molecular structure has now been observed. For larger molecules, simple theories do not seem to apply. For example, a series of constituents were bound to ethylene. The series included Ne, Ar, HF, HCl, NO, C<sub>2</sub>H<sub>4</sub>. In spite of the broad distribution of molecular structures and binding energies in this series, the vibrational predissociation lifetimes are all on the picosec. timescale. Recently, resolved rotational structure for the Ne:C<sub>2</sub>H<sub>4</sub> complex has been assigned as due to a hindered internal rotor.

**220. Studies in Spectroscopy and Chemical Dynamics**  
*A. Kuppermann, Chemistry & Chemical Engineering Division* **\$95,000**

Studies are being made on the low energy electron impact spectroscopy of molecules and free radicals of importance in combustion processes. The aim of these studies is to gain information about the low-lying electronically excited spin-forbidden states of these species and of their possible relevance to the reactions occurring in these processes. Studies are also being made on the dynamics of elementary reactions involving free radicals such as H or CH<sub>3</sub>. Free radicals are produced by pulsed laser photolysis of a parent halide and an abstraction product of the reaction of the free radical with molecules such as C<sub>2</sub>H<sub>2</sub> and HCN is detected by vacuum ultraviolet laser-induced fluorescence, using a second laser time-delayed with respect to the first one. The object of these studies is to obtain information about the translational energy dependence of the cross section of these reactions and its relation to activation energies. Such reactions are important in combustion processes.

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

**221. Energy Partitioning in Elementary Gas Phase Reactions**  
*R. Bersohn, Dept. of Chemistry* **\$70,000**

The dynamics of the elementary reactions A + BC → AB + C and A + BCD → AB + CD are being studied by a two laser experiment. One laser generates the reactive atoms A (carbon, hydrogen, fluorine or sulfur) by photodissociation of a suitable parent molecule. The second laser probes the internal state distribution of the products. The reactions of fluorine atoms with HI, ICN and I<sub>2</sub> have been studied. All iodine atoms products

are in the ground state. The conclusion is that fluorine atoms in their J = 1/2 state are unreactive. The hydrogen atom exchange reactions H + DX → HX + D are being studied (X = Cl, F). Spectroscopic techniques are being developed for studying the time dependence of atomic concentrations, in particular of different atomic sublevels.

**Cornell University**  
**Ithaca, New York 14853**

**222. Shock Tube Pyrolysis of Aromatic Hydrocarbons—Detection of Soot Precursors**  
*S.H. Bauer, Dept. of Chemistry* **\$51,000**

The objectives of the shock tube experiments are to determine the fragmentation patterns for structurally related di- and tricyclic aromatics, to measure the relative levels of soot produced, and to formulate semi-quantitative mechanisms for these processes. The experiments are performed in a single-pulse shock-tube with a coaxial laser beam absorption diagnostic. Gas chromatographic analyses are made of samples extracted from the downstream end of the shock tube. During the test time attainable with this configuration (700-900 μs) conversion of the shocked samples is kinetically limited. The shapes of the He/Ne transmission curves indicate that the attenuation of the beam is not due to loss by scattering from the final product, but to absorption by precursor species, the concentrations of which first rise and then decline due to subsequent reactions. For recording their extended absorption spectra, the He/Ne laser was replaced by a black-body source, and the photodetector by a 3/4m spectrometer equipped with a multi-element array detector-amplifier-computer system. This configuration, now being tested, will allow simultaneous recording of absorption spectra at 20 adjacent spectral intervals (each 5nm wide) with a time resolution of 20μs, for the entire duration of the shock-quench period.

**Georgia Institute of Technology**  
**Atlanta, Georgia 30332**

**223. Kinetic Study of Radical-Aromatic Hydrocarbon Reactions**  
*A.R. Ravishankara, Engineering Experimental Station* **\$64,700**

Improvements in the fundamental understanding of chemical reaction rates and pathways in radical-unsaturated and aromatic hydrocarbon reaction are the principal objectives of this program. Using the technique of (laser/flash) photolysis/ (resonance/laser induced) fluorescence, the absolute rate constant measurements for reactions of H, O, OH + aromatic and olefinic hydrocarbon are being carried out as functions of temperature and pressure. By judicious interpretations of observed kinetic isotope effects, the yield and identity of certain products, the temporal profiles of reactant and product concentrations, and the effect of pressure and scavenger concentrations on the rate coefficients, the reaction mechanisms for all the above reactions in the temperature range of 250-1100 K are being elucidated. Furthermore, studies on aromatic free radicals using laser induced fluorescence have been initiated. Information gained from these studies is expected to improve utilization of hydrocarbons both as combustibles and as feedstocks for synthetic fuel production, as well as increasing our understanding of hydrocarbon combustion.

## Howard University Washington, District of Columbia 20059

### 224. *Laser Studies of the Dynamics of Atom Molecule Reactions* W.M. Jackson, Dept. of Chemistry \$55,000

This project uses tunable dye lasers to measure the reaction rates of CN free radicals as a function of their internal energy. The project is based upon unique photochemical sources of internally excited CN radicals that can be produced from the laser photolysis of  $C_2N_2$ ,  $CICN$  and  $BrCN$ . Each of these compounds produce CN radicals that are rotationally or vibrationally hot. The amount of rotational and vibrational excitation depends upon the compound used, so that by measuring the rate constant with a particular source of CN, we hope to be able to obtain information about the effects of internal excitation on the rate constants for CN reaction. Studies have been completed on the effects of one quanta of vibrational energy on the rate constant for the reaction of CN with  $H_2$ ,  $O_2$ ,  $CO_2$ ,  $N_2$ ,  $HCN$ ,  $C_2N_2$ , and  $CH_4$ . These studies are currently being extended to include the effects of larger amounts of vibrational energy in the CN radical. Other studies have been started which demonstrate that the quenching of a combination of translational and rotational energy can produce vibrationally excited CN radicals with a high probability.

## Illinois Institute of Technology Chicago, Illinois 60616

### 225. *Theoretical Studies of Combustion Dynamics* J.M. Bowman, Dept. of Chemistry \$64,700

The objective of this research is to develop and apply approximate but accurate quantum mechanical methods to reactions of interest in gas phase combustion. Such a theory has been developed and applied to the reactions  $O(^3P) + H_2$ ,  $O + D_2$  and  $O + HD$  using an *ab initio* potential energy surface. Extension of the theory to treat diatom + diatom reactions has been made, and the first application will be to the  $OH + H_2$  reaction. A surface will be obtained from new *ab initio* calculations that are planned by Dr. Thom Dunning. Work is also underway to calculate the vibrational energies and lifetimes of  $HCO$  and  $HOCO$  using *ab initio* potential surfaces calculated by Harding. This work is based on a vibrational self-consistent field plus configuration interaction method developed here. The interaction of radiation with long-lived collision complexes is also being investigated, and preliminary calculations indicate that stabilization by stimulated emission may be feasible for small systems using lasers of moderate power.

### 226. *Studies of Combustion Kinetics and Mechanisms* D. Gutman, Dept. of Chemistry \$150,000

The purpose of the research is to gain new quantitative knowledge of the kinetics and mechanisms of the reactions of polyatomic free radicals which are important in hydrocarbon combustion processes. The free radicals are generated in a heated tubular reaction by the multiple-photon-induced decomposition of suitable precursors by a  $CO_2$  TEA laser. The ensuing reactions are monitored using a photoionization mass spectrometer capable of recording the time evolution of either reactants or products. The recombination of  $C_2H_5$  radicals is being studied in detail. Special procedures to determine their initial concen-

trations are also being developed. The reactions of alkyl radicals with molecules are being investigated as a function of pressure as well as temperature. In particular the  $C_2H_5 + O_2$  reaction is being studied from 300-1000K and from 0.4 to 8 torr total pressure. Details of mechanism changes at elevated temperatures are being obtained.

## Johns Hopkins University Baltimore, Maryland 21218

### 227. *Ionic Aspects of Soot Formation* W.S. Koski, Dept. of Chemistry \$68,000

By using tandem mass spectroscopic techniques, we are studying ion-molecule reactions that are of potential importance to combustion. It is observed that reactions such as  $C_2H_2^+ + C_2H_2$  and  $C_2H_4^+ + C_2H_4$  form condensation products (i.e.,  $C_4H_4^+$  and  $C_4H_8^+$  respectively) under binary collision conditions. On the other hand, the reaction  $C_2H_3^+ + C_2H_2$  does not form condensation products under the same conditions, although the ion  $C_4H_3^+$  is observed in flames. By running an electron bombardment ion source at high pressures, we find the  $C_4H_5^+$  ion when acetylene in the source is maintained at pressures greater than 0.5 torr. Other interesting ions such as  $C_4H_{11}^+$  and  $C_4H_4^+$  were also observed and are being studied by collision induced dissociation methods. Helium is used as a target gas. The interesting point about these ions made in this manner is that in any one of them not all of the carbon atoms are covalently bonded, but rather they are cluster ions in which an ion is bound to a neutral molecule by a small binding energy ranging from 0.1 eV to a few Kcal/mol. The binding energies of these clusters are being measured and their properties are being investigated.

## Kansas State University Manhattan, Kansas 66506

### 228. *Diffusion Flame Studies of the Chemical and Physical Mechanisms of Soot Formation From Aromatic and Substituted Aromatic Fuels* J.F. Merklin, C.M. Sorensen, Dept. of Nuclear Engineering \$60,000

We have continued our measurements of soot particulate sizes in flames using both the extinction/scattering ratio method and Photon Correlation Spectroscopy. The feasibility studies of size distribution measurements using PCS have begun. First, we have used model size distributions to create computer generated light-scattering data. These data have been fit in three different ways to determine the relative feasibilities of size distribution determinations. Second, we have measured PCS spectra from soot in a premixed  $CH_4/O_2$  flame. The data have been analyzed by these methods and have indicated width parameters in the range  $\sigma = 1.30 - 1.35$ . The same  $CH_4/O_2$  flame was chemically sampled and the sample was analyzed for the major and minor component concentrations. These results are in substantial agreement with the results previously reported in the literature. The isomeric distribution in the  $C_4$  hydrocarbons suggests that they are formed by the reaction of  $C_2$  hydrocarbon radicals.

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

- 229. Aromatics Oxidation and Soot Formation in Flames**  
*J.B. Howard, Dept. of Chemical Engineering* **\$90,600**

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 and 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 being used for gas species measurement. Soot particles are being studied by laser scattering and adsorption measurements in the flame and analysis of beam deposits. Net reaction rates calculated from these measurements are 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.

- 230. Depopulation Rates For Combustion-Related Species in Long-Lived ( $>100\mu\text{s}$ ) Vibrationally or Electronically Excited Levels**  
*J.L. Kinsey, R.W. Field, Dept. of Chemistry* **\$112,000**

In this project, a new technique called Stimulated Emission Pumping (SEP) is being used to study individual levels of polyatomic molecules with chemically significant amounts (up to  $\sim 3.5\text{eV}$ ) of vibrational excitation. Current effort focuses on the acetylene molecule, HCCH, in its electronic ground state ( $X^1\Sigma_g$ ). Individual rotation-vibration levels as much as  $2800\text{ cm}^{-1}$  above the vibrationless level are being studied to obtain information about the transition from regular to chaotic behavior in a molecular system. Parallel investigations are probing triplet levels of acetylene at  $\sim 45000\text{ cm}^{-1}$ , using Zeeman quantum beat spectroscopy and anticrossing spectroscopy. Among other things, these studies address the location of the  $\text{HCCH} \rightarrow \text{H} + \text{C}_2\text{H}$  dissociation limit from the variation of the density of triplet levels.

**National Bureau of Standards  
Washington, District of Columbia 20234**

- 231. Laser Studies of Chemical Dynamics at the Gas-Solid Interface**  
*R.R. Cavanagh, D.S. King, Center for Chemical Physics* **\$50,000**

This is an experimental program aimed at obtaining a detailed understanding of energy transfer and molecular dynamics occurring at the gas-surface interface. High resolution, pulsed laser techniques are used to probe the internal state distribution, molecular orientation, and state dependent angular flux and velocity distribution for free molecules which result from a variety of surface desorption processes. Current work utilizes laser excited fluorescence to probe the thermal desorption of nitric oxide from Ru(001), where the rotational state, spin-orbit state, lambda doublet species, and orientation effects are being determined. Doppler studies are being used to obtain rotational state

resolved angular flux and velocity distributions. This work is being extended to include a variety of thermal heating rates of the surface and a study of the influence of different substrates, such as Pt(111) and Pd(111).

- 232. Kinetics Data Base For Combustion Modeling**  
*W. Tsang, R.F. Hampson, Center for Chemical Physics* **\$63,000**

The aim of this research is to compile, evaluate, and publish information on the rate constants for single step chemical processes which are pertinent to the detailed description of hydrocarbon combustion processes. The plan of attack is to start with the simplest molecular systems, and then to expand into more complicated situations. All possible reactions are considered. Evaluation involves critical examination of experimental data, comparisons with analogous reactions, and expectations from theory. Where data do not exist, estimates are made. Results are presented on individual data sheets so as to permit periodic upgrading. Work on methane and ethane oxidation and pyrolysis have been completed. It should be noted that these reactions form a subset of all combustion processes. Further work will involve continuous updating and expansion into  $\text{NO}_x$ ,  $\text{CH}_3\text{OH}$ , and higher hydrocarbon systems.

**Princeton University  
Princeton, New Jersey 08544**

- 233. Comprehensive Mechanism For Combustion Chemistry: An Experimental and Numerical Study With Emphasis on Applied Sensitivity Analysis**  
*F.L. Dryer, Dept. of Mechanical and Aerospace Engineering* **\$90,000**

This program 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 bench marks 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 program necessitates a three-pronged approach: (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 the sensitivity analysis research of Rabitz at Princeton, the modeling efforts of Westbrook at Lawrence Livermore National Laboratory, and the fundamental kinetics program of Klemm and Michael at Brookhaven National Laboratory. The experimental aspects of the program are conducted in a flow reactor facility developed at Princeton which permits chemical kinetic observations at atmospheric pressure, in the temperature range of about 900 K to 1200 K, and for reaction times the order of 10 to 500 msec. The modeling aspects of the program 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 CO/H<sub>2</sub>/O<sub>2</sub> system, the formaldehyde pyrolysis and oxidation systems, the acetaldehyde pyrolysis and oxidation systems, and the ethanol pyrolysis and oxidation systems.

**234. Dynamical Studies of Molecular Systems**  
*H.A. Rabitz, Dept. of Chemistry* **\$134,000**

The research project has two parts consisting of studies in chemical kinetics and collision dynamics. In the first part on chemical kinetics, the research is concerned with the development and application of sensitivity analysis tools for the understanding of complex chemical mechanisms. Both time and spatially dependent problems are under study with a special emphasis on combustion phenomena. In the latter case, sensitivity techniques are being developed for probing the role of rate constants, transport coefficients, initial conditions, and boundary conditions on laboratory observables. The second part of the research in collision dynamics is concerned with phase space trajectory analysis and the development of collisional scaling relationships. Scaling has the goal of providing the theoretical framework for taking laboratory data to a more fundamental underlying level, such that it may be used again to produce new observable collision phenomena. A hierarchical approach to the theory of collisional scaling is being taken whereby the scaling relations may be employed with various levels of sophistication. Finally, a theory for the structural analysis of classical phase space trajectories is being developed. The approach allows for the calculation of a small number of structural constants which physically characterize the shape of the trajectory.

**Purdue University**  
**West Lafayette, Indiana 47907**

**235. Measurement of Radical Species Concentrations and Polycyclic Aromatic Hydrocarbon in Flames By Fluorescence and Absorption Via Tunable Dye Laser**  
*N.M. Laurendeau, Dept. of Mechanical Engineering* **\$94,000**

New quantitative laser fluorescence techniques are being developed to measure the concentrations of radical species and polycyclic aromatic hydrocarbons (PAH) in flames. Previously we have: (1) demonstrated laser-saturated fluorescence (LSF) measurements of OH and NH concentrations using a flat flame burner operated under a variety of flame pressures, temperatures, and equivalence ratios; (2) developed a potential technique for determining PAH concentrations in a vapor mixture; and (3) made the first reported fluorescence measurements of atomic hydrogen in flames using two-photon absorption. Recently, we have improved the calibration procedure and investigated the effects of non-uniform laser illumination for the LSF measurements. Current research includes: (1) laser-saturated CN and CH measurements; (2) PAH measurements using one- and two-photon excitation; and (3) two-photon measurements of atomic hydrogen and oxygen in flames.

**Rensselaer Polytechnic Institute**  
**Troy, New York 12181**

**236. Kinetic Measurements On Elementary Fossil Fuel Combustion Reactions Over Wide Temperature Ranges**  
*A. Fontijn, Dept. of Chemical & Environmental Engineering* **\$85,000**

This research project is aimed at providing kinetic data on important isolated elementary hydrocarbon molecule oxidation reactions. Emphasis is placed on measurements in the 1000-1800 K range, where accurate data are generally not available, but needed for development of improved fossil-fuel utilization methods. The high-temperature photochemistry (HTP) adaptation of the flash-photolysis resonance-fluorescence technique is further developed. Use is made of fast electronics, which allows rapid data taking and short residence times and of on-line microcomputer data smoothing procedures which minimize the number of flashes required. The first objects for study are reactions between O atoms and C<sub>2</sub> hydrocarbons.

**Rice University**  
**Houston, Texas 77251**

**237. Infrared Absorption Spectroscopy With Color Center Lasers**  
*R.F. Curl, Jr., Dept. of Chemistry* **\$65,000**

This research project is directed at the development of high sensitivity, high resolution methods for detecting and monitoring small free radical species which are thought to be important intermediates in combustion by means of infrared absorption spectroscopy using color center laser sources. Two new high sensitivity spectroscopic methods which can be combined with the long pathlengths obtainable with a White cell have been developed. One, a magnetic rotation technique for the suppression of source noise, provides a high sensitivity absorption spectroscopy which is selective for free radicals. The other, a high sensitivity spectroscopic method suitable for non-magnetic molecules, uses electro-optic tone modulation of the color center laser infrared output. For the latter technique, a CdTe electro-optic modulator was specially designed and has recently been successfully tested. Earlier, the magnetic rotation method was used to observe and assign the electronic spectrum of C<sub>2</sub>H in a discharge through argon over polyacetylene. In the continuation of this work, efforts will focus upon the identification of other radical species present in the discharge over polyacetylene as evidenced by as yet unassigned Q-branches. When observed by the tone modulation technique, the entire structure of these band fragments should be revealed.

**238. Supersonic Metal Cluster Beams**  
*R.E. Smalley, Dept. of Chemistry* **\$75,000**

Laser vaporization of a metal target within a pulsed supersonic nozzle is used in this research to prepare beams of transition metal clusters. This new technique (developed in the previous year of this DOE contract) is perfectly general for even the most refractory metals (e.g., tungsten), and readily provides an intense source of bare metal clusters cooled to internal temperatures on the order of 5 K. Current research with this new source centers around the spectral study of small transition metal clusters, in order to obtain accurate and definitive measurements of the metal-metal bond (bond length, dissociation energy, electronic structure, bond angles, vibrational frequencies, etc.). Metal clusters studied thus far include Cr<sub>2</sub>, V<sub>2</sub>, Ni<sub>2</sub>, Cu<sub>2</sub>, Cu,

and Mo<sub>2</sub>. The results in the case of Cr<sub>2</sub> and V<sub>2</sub> indicate that the metal-metal bond in this region of the transition series is dominated by strong 3d orbital interaction, resulting in extremely short bond lengths. Nickel and copper, on the other hand, are found to be bound mostly through the 4s orbitals.

### **SRI International** **Menlo Park, California 94025**

- 239. Combustion Research Program: Flame Studies, Laser Diagnostics, and Chemical Kinetics**  
*D.R. Crosley, Molecular Physics*      **\$114,900**  
*Lab.*

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<sub>6</sub> is rapidly heated by a pulsed CO<sub>2</sub> laser, with time-resolved LIF measurements of radical concentrations and temperature. Measurements of the OH + C<sub>2</sub>H<sub>2</sub> 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 measurements on OH + CH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, and NH<sub>3</sub> have also been made. Calculations on the H + N<sub>2</sub>O reaction and CH<sub>3</sub> + CH<sub>3</sub> recombination show bound intermediates and very different rate constant expressions from those currently used. The LIF spectroscopy of the A<sup>3</sup>Pi<sub>i</sub>-X<sup>3</sup>Σ<sup>-</sup> system of NH in a flow system has yielded lifetimes and transition probabilities, and the LIF flame spectra of NH<sub>2</sub> in NH<sub>3</sub>/O<sub>2</sub>/N<sub>2</sub>O flames is being catalogued.

### **Stanford University** **Stanford, California 94305**

- 240. Studies of Combustion Gas Spectroscopy Using Tunable Lasers**  
*R.K. Hanson, Dept. of Mechanical Engineering*      **\$55,000**

Objectives of this research are: (1) the measurement of fundamental spectroscopic parameters (absorption coefficients, band or oscillator strengths, and collision widths) for critical combustion species, particularly pollutants and radicals; and (2) the development of tunable laser absorption and fluorescence techniques for species measurements in studies of chemical kinetics. 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, CO, OH, NH, CH, NCO, and water vapor. Measurements are made over a range of conditions in a controlled-temperature absorption cell, in the post-flame region of a flat flame burner, and in a shock tube.

- 241. The Kinetics of Some Reactions of HCN At High Temperature**  
*R.K. Hanson, C.T. Bowman, Dept. of Mechanical Engineering*      **\$70,000**

The objective of this research project is to obtain high-temperature kinetic data for reactions involving HCN and the CN radical. These data are relevant to the formulation of reaction mechanisms for pollutant formation in flames. Reactions of interest include: (1) the thermal decomposition of HCN; and the reactions of HCN with CN, H, O, and OH; (2) the thermal decomposition of C<sub>2</sub>N<sub>2</sub>; and (3) the reactions of CN with O and O<sub>2</sub>. 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 empirical models.

### **State University of New York/Buffalo** **Amherst, New York 14226**

- 242. Multiphoton Interactions in Molecules With Picosecond Laser Pulses**  
*H.S. Kwok, Dept. of Electrical and Computer Engineering*      **\$64,000**

High power CO<sub>2</sub> laser pulses are employed in this research program to study the multiphoton behavior of polyatomic molecules. During the past year, we have carefully measured the excitation of SF<sub>6</sub> by picosecond laser pulses with various durations. A second laser was added to the experimental setup to pre-heat the SF<sub>6</sub> molecules into the quasicontinuum of vibrational states. It was found that the multiphoton excitation depended only on the intensity of the laser pulse, for durations between 38 and 150 ps. This indicates a breakdown of the energy fluence scaling law and points directly to coherent excitation in the quasicontinuum. It is first firm experimental evidence of coherent excitation of any system in the presence of strong intramolecular damping. We have developed an N-level Bloch equation model that includes both coherent and incoherent excitation in the quasicontinuum. The experimental data are commensurate with slow intramolecular energy transfer and increasing oscillator strength as the molecular is excited. Other molecules will be tested using the same techniques.

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

- 243. Multiphoton Ionization Spectroscopy and Photochemistry of Transient Species**  
*P.M. Johnson, Dept. of Chemistry*      **\$65,000**

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 which are 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 benzene as well as the radical CCl.

**University of Arizona**  
Tucson, Arizona 85721

- 244. Experimental Studies of the Ionizations and Bonding of Small Molecules Attached to Transition Metals**  
D.L. Lichtenberger, Dept. of Chemistry **\$77,000**

This research project focuses on experimental investigation of the electronic mechanisms of bond activation of small molecules by transition metals. The primary experimental technique is gas-phase photoelectron spectroscopy, utilizing HeI, HeII, and X-ray excitation sources. Breakthroughs have been made with the HeI source in observing detailed vibrational structure in metal ionizations. An improved HeII source design has proven to be especially valuable in understanding the valence ionizations of organometallic molecules. Gas phase core photoelectron spectroscopy has been developed, and has shown important correlations between core and valence ionizations shifts. The systems receiving most attention involve metal interactions with small organic species that are proposed intermediates in water-gas shift and Fischer-Tropsch catalysis, such as alkyls, alkenes, alkynes, methylenes, and vinylidenes. An important new study involves investigation of metal-alkyl complexes that represent intermediate stages of carbon-hydrogen bond breaking and formation. We have also recently acquired new state-of-the-art instrumentation for applying these photoelectron techniques to the study of molecules on surfaces. This will allow development of a more complete relationship with surface chemistry and catalysis.

**University of California/San Diego**  
La Jolla, California 92093

- 245. Shock-Tube Studies of Important Combustion-Reaction Steps Involving Radicals**  
K.G.P. Sulzmann, Energy Center **\$63,500**

The aim of this research is twofold: (1) the use of shock-tube techniques for the rapid introduction of known intermediate and radical concentrations into a combustion environment, in which the individual interactions of these species with other reactants and intermediates can be separated or enhanced for meaningful rate measurements of individual or sub-groups of reaction paths relevant to hydrocarbon combustion; and (2) the use of *in situ* quantitative spectroscopic measurement techniques, for the determination of required species concentration-time histories. As a first step, the only partly understood fate and kinetics of the CH<sub>3</sub>-radical is investigated during its donor-pyrolysis, and its interactions with O<sub>2</sub> and O-atoms behind reflected shock-waves by using argon-diluted CH<sub>3</sub>CO<sub>2</sub>CH<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>, CH<sub>3</sub>COCH<sub>3</sub> and/or CH<sub>3</sub>N<sub>2</sub> as methyl radical donors. Oxidation reactions are initiated by admixing either O<sub>2</sub> or N<sub>2</sub>O as an O-atom donor. Quantitative spectroscopic data are obtained by infrared emission (2 channels), by infrared HeXe-laser absorption at 3.508μ, by visible ultraviolet emission (10 channels), and/or by vacuum-ultraviolet absorption.

**University of Chicago**  
Chicago, Illinois 60637

- 246. Topics in Finite Time Thermodynamics**  
R.S. Berry, James Franck Institute **\$72,000**

The term "finite time thermodynamics" refers to the extension of traditional thermodynamics to the description of systems and processes whose constraints include finite times or nonzero rates of operation. In particular, the term refers to the determination of the extremal performance and the paths that would yield that performance, when the constraints of finite-time operation must be met. The progress of this group since the last report has included: (1) the theoretical description and elaboration of a new type of engine, based on a dissipative process; (2) an analysis of space heating under periodic illumination conditions (as with the diurnal variations of solar systems), with control by (nonenergy-consuming) variation of insulation; an analysis of the entropy production by such a system; (3) the exploration of geometric formulation of thermodynamics based on the metric introduced by Weinhold, including the proofs of relations between dissipation in a finite-time process and the "length" of the path for that process calculated by Weinhold's metric; and (4) the further extension of the concept of availability (exergy) to processes operating in finite time, and the application of this extended concept to extraction of work from a system not initially in internal equilibrium.

- 247. Laser Induced Chemical Reactions and Laser-Collision Processes**  
J.C. Light, James Franck Institute **\$70,000**

Laser induced chemical processes of several types have been observed experimentally. Our research program is to develop theoretical methods to examine some of these and related processes. Methods to do exact 3-D quantum calculations of single photon photodissociation of triatomic molecules have been developed and applied to models of HCN and ICN. A new representation of the problem (discrete variable representation) simplifies the calculation considerably by taking advantage of the localization of the initial state. These techniques are now being applied to the related problems of dissociative attachment in electron molecule collisions (e<sup>-</sup>+F<sub>2</sub>, e<sup>-</sup>+CO<sub>2</sub>) and to dissociation by photoemission from Rydberg states H<sub>3</sub><sup>+</sup>(Rydberg) → H<sub>2</sub>+H+hν. Realistic calculations of multiphoton dissociation of O<sub>3</sub> in intense laser fields are being done using a realistic internal state structure and our recently developed rotating frame transformation.

**University of Colorado**  
Boulder, Colorado 80309

- 248. Laser Photoelectron Spectroscopy Of Ions**  
G.B. Ellison, Dept. of Chemistry **\$165,000**  
(18 mo.)

Laser photoelectron spectroscopy has been used to study a number of simple negative ions. Our experiments produce direct, reliable thermodynamic information such as electron affinities, radical and ion heats of formation, and bond dissociation energies. These are crucial data required for an understanding of combustion processes. We have completed careful studies of HNO<sup>-</sup>, DNO<sup>-</sup>, CH<sub>2</sub>CCH<sup>-</sup>, CH<sub>2</sub>CCD<sup>-</sup>, CD<sub>2</sub>CCH<sup>-</sup>, CCO<sup>-</sup>, HCCO<sup>-</sup>, and DCCO<sup>-</sup>. We have just finished work on CH<sub>2</sub>CN<sup>-</sup>,

$\text{CD}_2\text{CN}^-$ ,  $\text{CH}_2\text{NC}^-$ , and  $\text{CH}_3\text{CHCN}^-$ . Proposed research centers on polymeric carbon ions ( $\text{C}_n^-$ ), allyl anion ( $\text{CH}_2 = \text{CH}-\text{CH}_2^-$ ), and  $\text{CO}_2^-$ .

**249. Time-Resolved Studies of Free Radicals and Laser-Initiated Chain Reactions**  
S.R. Leone, Dept. of Chemistry **\$70,000**

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 combust-ing 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. A multiple vibrational state analysis has been developed and applied to the extraction of rate information for very slow chain reactions.

**University of Illinois**  
Chicago, Illinois 60680

**250. Kinetics of Elementary Atom and Radical Reactions**  
R.J. Gordon, Dept. of Chemistry **\$70,700**

The objectives of this research are to measure the reaction rates and to study the dynamics of elementary gas phase reactions, using sensitive, real time techniques to eliminate systematic errors. One system being studied is  $\text{O} + \text{H}_2$ ,  $\text{D}_2$  and  $\text{HD}$ . 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 intramolecular branching ratio for  $\text{O} + \text{HD}$  is being determined by using laser-induced fluorescence to measure the relative concentrations of  $\text{OH}$  and  $\text{OD}$  products. In a separate study, the relaxation of highly excited molecules is being studied by using a  $\text{CO}_2$  laser to excite a donor molecule while detecting IR fluorescence from a receptor molecule. Studies of  $\text{SF}_6 + \text{N}_2\text{O}$  and  $\text{SF}_6 + \text{NO}$  yield the VV transfer rate as a function of  $\text{SF}_6$  excitation. The observation of a slower decay rate at higher excitation levels indicates the existence of an energy storage mechanism in the  $\text{SF}_6$  molecule.

**251. Laser Schlieren, Shock Tube Studies of High Temperature Hydrocarbon Pyrolysis Rates**  
J.H. Kiefer, Dept. of Chemical Engineering **\$65,000**

This project investigates the rates and mechanism of fuel pyrolysis reactions of importance in combustion at very high temperatures. Experiments use the shock tube in conjunction with laser-schlieren diagnostics capable of providing an accurate measure of initiation rates with 0.1  $\mu\text{s}$  resolution as well as some secondary rates. Rates and mechanisms for the pyrolysis of propane, propene, ethane, ethylene/acetylene, butadiene, benzene, and toluene have been investigated. The ethane study strongly indicates that methyl-methyl reactions, other than recombination, do not occur at significant rates to 2700K. The butadiene study suggests a low heat of formation for vinyl radical ( $\Delta H_{f,298}^\circ < 65$  kcal/mole), and an estimate for the high-T vinyl radical dissociation rate, a rate of considerable importance in combustion modeling.

**University of Kansas**  
Lawrence, Kansas 66045

**252. Molecular Design Principles For Biomimetic Solar Energy Conversion Systems**  
G.M. Maggiora, Dept. of Biochemistry **\$89,400**

*Ab initio* quantum mechanical and empirical potential function procedures are being applied in an investigation of the physico-chemical factors underlying biological and biomimetic solar energy conversion, and these factors will be used to develop a set of molecular design principles, which will enable chemists to formulate structures of potential biomimetic photoconversion systems possessing specified properties more efficiently. Current studies are directed towards porphyrin dimer and trimer systems, especially hetero-dimers. Preliminary results indicate the existence of low-lying, non-radiative charge-transfer states in magnesium porphine-porphine dimers which may be sufficiently long-lived to facilitate electron transfer from these dimers to appropriate acceptors. The results are being further evaluated with regard to the effects of intermolecular geometry and microenvironment on the location and character of the charge-transfer states. Studies are also continuing on the evaluation of possible molecular candidates for the P700 and P680 photoactive species in the photoreaction centers of green plants. In addition, the development of new and improved theoretical methodologies and algorithms are being actively pursued.

**University of Minnesota**  
Minneapolis, Minnesota 55455

**253. State-to-State Dynamics of Molecular Energy Transfer**  
W.R. Gentry, C.F. Giese, Depts. of Chemistry and Physics **\$80,000**

A novel pulsed molecular beam instrument has been constructed for the study of state-to-state vibrational and rotational energy transfer in collisions of atoms and molecules. The results are expected to lead to an understanding of molecular energy transfer on a microscopic level, including the dependence of energy transfer processes on the vibrational and translational energies of the colliding molecules. The first experiments measured the kinetic energy dependence of the vibrational excitation cross sections for  $\text{I}_2 + \text{He}$  collisions. Similar measurements have now been performed for  $\text{I}_2 + \text{D}_2$  and  $\text{I}_2 + \text{Ne}$  collisions, in order to explore the effects of mass and features of the potential energy surface on the excitation dynamics. These experiments are being extended to other systems, including mode-specific excitation of the polyatomic molecules aniline and p-difluorobenzene.

**254. Variational Transition State Theory**  
D.G. Truhlar, Dept. of Chemistry **\$70,000**

This research project is an attempt to develop and implement new methods for calculating rate coefficients for chemical reactions from potential energy surfaces. Emphasis is being placed on gas-phase atom-transfer reactions, which are an important reaction type in combustion and atmospheric systems, as well as being of fundamental interest. We are also studying the effect of vibrational excitation of the reactants on chemical reaction rates, and we are studying kinetic isotope effects. A very important aspect of our studies is the inclusion of quantal effects in

reaction rate calculations, with special emphasis on tunneling (barrier penetration), and on the dependence of vibrational frequencies on the reaction coordinate. We are developing methods to model the potential energy surfaces for simple reactions and also to utilize *ab initio* reaction-path Hamiltonians in our calculations. Examples of our applications to reactions important in combustion are  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ , and  $\text{OH} + \text{O} \rightarrow \text{H} + \text{O}_2$ , and  $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$ .

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

- 255. Identification and Temporal Behavior of Radical Intermediates Formed During the Combustion and Pyrolysis of Gaseous Fuels**  
*R.D. Jr. Kern, Dept. of Chemistry* **\$60,000**

The practical and environmentally acceptable use of fossil fuels containing aromatic hydrocarbons in furnaces and engines is dependent upon the control of soot formation. The chemical sequence of reactions which lead to soot are being investigated by recording the product profiles generated during the pyrolyses of toluene, benzene, allene, butadiene, and acetylene. The experimental technique utilized involves the dynamic sampling of the reflected shock zone by time-of-flight mass spectrometry. Data have been obtained over a wide range of temperature and fuel concentrations. Computer modeling has successfully fit many of the experimental profiles. The major findings are: (1) the dominance of the ring fragmentation routes as opposed to ring condensation steps in the pyrolyses of toluene and benzene; (2) the limited amount of ring formation observed in the decompositions of allene and butadiene; and (3) the absence of ring species formed during the polymerization of acetylene.

### University of Rochester Rochester, New York 14627

- 256. Low Energy Ion-Molecule Reactions and Chem-ionization Kinetics**  
*J.M. Farrar, Dept. of Chemistry* **\$70,000**

Molecular beam reactive scattering measurements of proton transfer reactions of the flame cations  $\text{HCO}^+$  and  $\text{H}_3\text{O}^+$  with neutral molecules present in hydrocarbon flames are being carried out to understand the dynamics of ionic processes occurring in flames. Measurements of product angular and kinetic energy distributions yield energy disposal in reactive collisions, inferences concerning preferred collision geometries, and in favorable cases, determination of specific quantum states of nascent reaction products. Proton transfer reactions to the substrates  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , and  $(\text{CH}_3)_2\text{C}=\text{O}$  have been studied, indicating direct reaction dynamics. Unimolecular decay channels of protonated products are studied and decays involving bond cleavage, 1,3-hydrogen atom shifts, and elimination of molecular hydrogen across the C-O bond have been observed. In the latter case, variations of proton donor modifies the parent ion internal state distribution; such observations are being employed to assess the role of tunneling through the exit channel barrier in the elimination process. Work in progress involves hydride transfer reactions of  $\text{CH}_3^+$  as well as studies of carbon cations,  $\text{C}^+$ , with small hydrocarbons.

### University of Utah Salt Lake City, Utah 84112

- 257. Study of Combustion and Flame Processes Initiated By IR Laser-Induced Absorption**  
*W.A. Guillory, Dept. of Chemistry* **\$80,000**

The phenomenon of infrared multiple-photon absorption (IR MPO), subsequently leading to excited and ground state dissociation products, simulates non-equilibrium processes occurring in flames and other combustion systems. Using visible and UV laser-induced fluorescence diagnostics as probes of the reaction zone, highly sensitive time and wavelength resolved spectroscopy allow detailed determination of the mechanisms and energetics of a given system. The reactions of vibrationally excited ground electronic state CH and OH (produced by IR MPO) with  $\text{O}_2$ ,  $\text{N}_2$ , NO, and aliphatic and aromatic hydrocarbons are being studied. Also being studied is the efficiency and means of production, via IR MPO, of CH and OH from various precursors. New techniques, such as multi-photon absorption fluorescence, are being implemented to study amounts of and energy states of reactive and product species ( $\text{CH}_2$ ,  $\text{CH}_3$ , C, and so forth). Discrete level and quasicontinuum energy transfer and relaxation in propynal, glyoxal, and methylglyoxal are also being studied.

### University of Wisconsin Madison, Wisconsin 53706

- 258. Unimolecular Reaction Dynamics**  
*F.F. Crim, Dept. of Chemistry* **\$52,400**

This program 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 provides a direct measure of the unimolecular reaction rate constant and, in favorable cases, the energy partitioning in the products. This work includes excitation of both CH and OH overtone vibrations and product detection using both visible chemiluminescence and laser induced fluorescence. The most extensive recent results are on hydrogen peroxide (HOOH) and its partially deuterated analogue (HOOD) initially excited with five ( $5\nu_{\text{OH}}$ ) or six ( $6\nu_{\text{OH}}$ ) quanta of stretching in the OH bond. These detailed studies critically test statistical theories of unimolecular reactions and provide data on the dynamics of isolated molecules which are potentially useful in understanding atmospheric chemistry, combustion processes, and laser induced reactions.

### Wright State University Dayton, Ohio 45435

- 259. Direct Determination of Atom and Radical Concentrations in Thermal Reactions of Hydrocarbons and Other Gases**  
*G.B. Skinner, Dept. of Chemistry* **\$58,400**

The general goal of this research is to study the kinetics of the atom and free radical reactions that are important in combustion reactions by following the appearance and disappearance

of H, O, OH, and other such combustion intermediates. H, D, and O atoms are currently being measured in shock tube experiments using resonance adsorption spectroscopy in the vacuum ultraviolet. Measurements made recently involve pyrolysis of butadiene, and analysis for both H and D in pyrolysis of partially deuterated propene. A series of experiments in which H Atoms produced by dissociation of neopentane or toluene react with acetylene-d<sub>2</sub> has been carried out to study the formation and stability of the vinyl radical. Measurements of both H and D concentrations help to clarify the reaction mechanisms. The shock tube has recently been modified to extend the range of total pressures from 3 atmospheres down to 0.4 atmospheres, so the dependence of reactions on total pressure can be more effectively studied.

**Yale University**  
New Haven, Connecticut 06520

- 260. Simultaneous Multipoint Measurements of Density Gradients and Temperature in a Flame**  
R.K. Chang, B.T. Chu, M.B. Long, **\$68,000**  
Section of Applied Physics and  
Dept. of Mechanical Engineering

The main thrust of this research program is directed toward developing new *in situ* optical techniques for characterizing turbulent reactive and nonreactive flows. Central to the technique developed in mapping two-dimensional concentration distributions in such flows is the use of a low-light-level television camera capable of detecting the scattered radiation from 10<sup>4</sup> discrete volumes in the flow. Such measurements, while instantaneous, can be recorded only at ~30 frames/s which is too slow to follow the temporal evolution of turbulent structures and flame sheets. We have recently succeeded in increasing the effective frame rate of our existing slow camera 70-fold to ~2000 frames/s by inserting a rotating mirror in our detection system and synchronizing the laser pulse rate with the rotational velocity of the mirror. Further increase of the effective frame rate is being explored. In another study, we have demonstrated that broadband rotational CARS is a potentially viable technique for single-pulse flame temperature measurements and that simultaneous temperature and species measurements with rotational CARS from many spatially resolved volume elements along a cylindrical line in room-temperature gases are feasible.

## Atomic Physics

**Atlanta University**  
Atlanta, Georgia 30314

- 261. Theoretical Investigation of Electron-Ion Interaction**  
A.Z. Msezane, Dept. of Physics **\$50,000**

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<sup>3+</sup>, important in CTR plasmas. Also, total and differential cross sections for electron impact excitation of Cd 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.

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

- 262. Collisional Detachment of Negative Ions**  
R.L. Champion, L.D. Doverspike, **\$80,000**  
Dept. of Physics

The fundamental goals of these experimental studies are to determine various cross sections, and to develop a general understanding of the collisional dynamics for systems which 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 upon developing an understanding of the role of competing product channels in negative ion-molecule collisions and upon delineating the various collisional processes that may occur in collisions of negative ions with molecular targets. Systems which are being investigated include hydrogen, deuterium, oxygen and halogen negative ions in collisions with hydrogen, deuterium, halogen molecules, O<sub>2</sub>, HCL, N<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub>. The experimental results are coupled with theoretical models to provide a basis for understanding the role of negative ions in various environments.

**Cornell University**  
Ithaca, New York 14853

- 263. Experimental Study of Interactions of Highly Charged Ions With Atoms At keV Energies**  
V.O. Kostroun, Nuclear Science **\$180,000**  
and Engineering Program

Experimental and theoretical interest in interactions of low energy highly charged ions with atoms or ions is due to the relevance of such interactions to controlled thermonuclear fusion research and to the interesting nature of the fundamental processes involved. This program centers around experimental investigations of interactions of highly charged ions and atoms at low energies, and consists of two parts. One involves atomic physics experiments and source studies and development using a small electron beam ion source (EBIS) called CEBIS I. The other, initiated in August 1983, involves the design, construction, and development of a larger superconducting solenoid version called CEBIS II. CEBIS I is used to investigate low energy charge transfer to multiply charged ions, in particular to measure partial cross sections for population of specific states of the projectile as a function of its energy for C<sup>q+</sup>, N<sup>q+</sup> and O<sup>q+</sup> (q ≥ 3) colliding with molecular hydrogen and helium in the 0.05

qkeV to 5 qkeV range. Specific states of the projectile populated in the collisions are selected by high resolution energy gain spectroscopy. The immediate goal of CEBIS II will be to generate a usable,  $\sim 3$  qkeV beam of  $\text{Ar}^{18+}$ . Longer range goals include optimization of the source and gradually upgrading it to handle a 25 kV, 1 A electron beam which could be used to produce He-like xenon.

**Harvard University**  
Cambridge, Massachusetts 02138

**264. Theoretical Studies of Highly Ionized Species**  
*A. Dalgarno, Harvard-Smithsonian* \$130,000  
*Center For Astrophysics*

Studies are made of collisions of multiply-charged ions with neutral gas affect the ionization structure, thermal balance, radiation losses, and ion transport in plasmas containing a neutral component. Because the products of the collisions radiate, they can be detected and thereby provide unique diagnostic probes of the environment. We have extended our calculations of the efficiencies of the processes so that their accuracy can be assessed by comparison with experimental data, which are now becoming available. We have made estimates of charge transfer into individual fine-structure states because observations of astrophysical objects show that the separate emission lines can be distinguished readily. We have also explored collisions of positive and negative ions.

**Jackson State University**  
Jackson, Mississippi 39217

**265. Spectroscopy of Trapped Molecular Ions**  
*J. Perkins, G. Miller, Dept. of* \$55,000  
*Chemistry*

The goal of this project is to provide spectroscopic data that will document those characteristics of molecular ions responsible for the large cross sections accompanying ion-molecule reactions. Using laser induced fluorescence (LIF), energy level and lifetime measurements are made of various small molecular ions (e.g.,  $\text{O}_2^+$ ,  $\text{CO}^+$ ,  $\text{CH}^+$ , and  $\text{CH}_2^+$ ). The ions are prepared by fragmentation of parent neutral gases through electron impact using a Pierce-type pulsed electron gun. The ions are mass selected by, and trapped in, a quadrupole ion trap long enough to carry out the spectroscopic measurements. Attempts are made to study intramolecular and intermolecular energy exchange involving electronic, vibrational, and rotational motions of these ions. Light intensity measurements are made using a dye laser, and the results are used to determine excited state lifetimes in the order of tens of milliseconds.

**Kansas State University**  
Manhattan, Kansas 66506

**266. Atomic Physics of Strongly Correlated Systems**  
*C.-D. Lin, Dept. of Physics* \$86,000

This project is directed toward the understanding of correlations of two-electron atoms in hyperspherical coordinates, and the development of practical codes for computing inelastic cross sections in ion-atom collisions. A complete classification scheme for doubly excited states is being developed. Dipole selection

rules for photoabsorption are being investigated. The modified atomic-orbital model (AO+) and the triple center AO expansion method are generalized to include excitation, charge transfer, and ionization processes for calculating inelastic ion-atom collisions at intermediate and low velocities.

**267. Atomic Physics With Highly Charged Ions**  
*P. Richard, Dept. of Physics* \$530,000

High velocity, highly charged ions produced by the 6 MV KSU tandem Van de Graaff are used to study charge transfer, ionization, and excitation in ion-atom collisions. Electron capture by highly-charged ions, produced as recoils from fast-ion bombardment of gases is studied at very low projectile velocities. During this contract year, electron capture from lithium by very low-energy protons and helium ions has been studied. Energy-gain spectroscopy has been performed for slow, highly charged projectiles on rare gas targets. Cross sections for electron capture by similar projectiles from an atomic hydrogen target have been carried out. The production of short-lived multiply-charged molecular species from a recoil source has been studied. Electron capture by fast K-vacancy-bearing metastable projectiles from rare gas targets has been studied. Investigation of quasi-resonant K-vacancy transfer has been extended downward in velocity revealing informative further structure in the impact-parameter dependence of the process. The Thomas peak in the angular distribution of electron-capturing protons from molecular hydrogen was observed and theoretical work completed for a quantitative understanding of the effect.

**Louisiana State University**  
Baton Rouge, Louisiana 70803-4001

**268. Electron Collisions With Positive Ions**  
*R.J.W. Henry, Dept. of Physics and* \$57,000  
*Astronomy*

The fundamental goal of this project is to delineate the important physical processes which govern electron impact excitation processes for impurity ions in high temperature plasmas of interest in the 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  $\text{Ti}^{+3}$  and are in good agreement with known measurements. Differential electron scattering cross sections for inelastic excitation of  $\text{Zn}^+$  are calculated at energies between 15eV and 100eV. Agreement of theory with experiment at 75eV is excellent over the measured angular range of  $4^\circ$  to  $16^\circ$ . Inelastic electron impact cross sections are calculated for  $\text{Mg}^+$  and  $\text{Al}^{++}$ . Calculations give good agreement with recent measurements from crossed-beam experiments.

**National Bureau of Standards**  
Washington, District of Columbia 20234

**269. Electron-Atom Collision Studies Using Optically State Selected Beams**  
*R.J. Celotta, M.H. Kelley, Division* \$62,000  
*of Radiation Physics*

Coherence and correlation techniques in atomic collision experiments are being used to improve our understanding of the interactions important in the atomic collision process. Production and detection of spin polarization in free electron beams and laser optical pumping methods for the production of polarized atomic beams have been used to study electron-atom collisions using quantum state selected beams. Such studies provide the maximum allowable information about the interaction, and require an experimental arrangement only slightly more complicated than a conventional crossed beam scattering apparatus. A scattering apparatus which uses optically selected beams capable of very general studies of collisions between spin polarized electrons and spin polarized atoms has been constructed. This facility will be used to make a comprehensive study of the role played by electron spin in electron-atom interactions. In particular, for alkali atoms, the exchange interaction and the spin-orbit interaction in elastic, inelastic, and superelastic collisions will be examined. The studies of electron correlation in ionizing collisions near threshold will be continued.

**270. Atomic and Molecular Collision Processes**  
*D.W. Norcross, Quantum Physics Division* **\$93,000**

The focus of this project is the physics of low energy collisions of electrons with atoms, ions, and molecules, with an emphasis on detailed computational studies. High precision calculations for elastic scattering by neutral helium are being extended to near-threshold excitation. Work on electron-impact excitation of He-like ions was extended to  $\text{Ca}^{+18}$ . All important physics (close-coupling, target fine-structure, autoionization, dielectronic recombination) is included. A new parameter-free correlation-polarization model for molecular scattering based on free-electron-gas theory has been tested for several molecules, including  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{HCl}$ . Calculations of vibrationally elastic scattering by  $\text{HCN}$ , and of vibrational excitation of  $\text{HCl}$ , in the adiabatic-nuclei approximation, with an exact treatment of exchange, have been completed. Code development that will lead to complete vibrational close-coupling calculations, with exact exchange, is in progress.

**New York University**  
**New York, New York 10003**

**271. Energy-Related Atomic and Molecular Structures and Scattering Studies**  
*B. Bederson, Dept. of Physics* **\$85,000**

A project to study atomic and molecular interactions with static and dynamic (laser) fields is in progress. An additional effort is under way to study interactions of electrons with highly polar molecules. This work is partly motivated by the goal of understanding the role played by long-range forces in atomic and molecular physics. We have just completed a study of the electric dipole polarizabilities of all the alkali-halide dimers and of atomic indium. We have also obtained, for the first time, tentative values for monomer polarizabilities of several alkali-halides. Collision experiments executed involve scattering of slow electrons ( $\sim 0.5$  to  $20$  eV) by alkali-halide molecules and their dimers. Absolute values of effective cross sections for  $\text{CsBr}$ ,  $\text{CsCl}$ ,  $\text{KI}$ ,  $\text{RbBr}$  and  $\text{RbCl}$  have been obtained. These can be directly compared with computations by folding the latter into our known apparatus parameters. A systematic study of

similar cross sections using other molecules possessing a range of dipole moments is also in progress. Extension of the scattering measurements to dimers, trimers, and to state-selected monomers, is also under way.

**Rice University**  
**Houston, Texas 77005**

**272. Theoretical Atomic and Molecular Sciences**  
*N.F. Lane, Dept. of Physics* **\$110,000**

Theoretical quantum-mechanical and semi-classical 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) excitation and excitation-transfer in slow collisions between highly-excited atoms and molecules; (4) ro-vibrational excitation in electron-molecule radiative and non-radiative charge-transfer collisions; and (5) related topics.

**Smithsonian Astrophysical Observatory**  
**Cambridge, Massachusetts 02138**

**273. Measurements of Ionization Balance Parameters in Atomic Ions**  
*J.L. Kohl, Division of Atomic and Molecular Physics* **\$100,000**

The purpose of this research project is to measure the basic atomic parameters that govern the charge distribution of atomic ions in high temperature plasmas. The present research efforts are directed toward measurements of absolute cross sections for dielectronic recombination of a multiply charged atomic ion and a free electron. This process is believed to dominate the ionization balance of impurity ions in potential controlled thermonuclear plasmas. The measurements utilize inclined electron and ion beams and, in the experiments, ion-photon pairs of recombined ions and stabilizing photons from individual dielectronic recombination events are measured in coincidence to ensure the correct identification of the detected process. The present activity is a measurement of the dielectronic recombination cross section for  $\text{C}^{3+}$ . Several modifications have been made to the experiment to reduce the accidental coincidence rate to an acceptable level.

**SRI International**  
**Menlo Park, California 94025**

**274. Studies of Autoionizing States Relevant to Dielectronic Recombination**  
*T.F. Gallagher, Molecular Physics Lab.* **\$77,000**

The goal of this project is the study of doubly excited atomic states of alkaline earth atoms which lie above the lowest ionization limit and thus autoionize. This is of practical importance since dielectronic recombination of ions and electrons via autoionizing atomic states plays an important role in energy loss

from tokamak plasmas. Both the intrinsic properties of the atoms and the effects of external fields are investigated. The approach employed is multistep laser excitation of atoms in a thermal beam, followed by subsequent detection of the ions and electrons produced by autoionization. The high resolution of the laser affords an excellent spectral probe of the autoionizing levels, and energy analysis of the ejected electrons allows the final state to be unambiguously determined. In fact, this approach is precisely the inverse of dielectronic recombination. We are thus able to probe in detail many of the phenomena associated with dielectronic recombination in plasmas.

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

**275. *Multilevel Relaxation Phenomena and Population Trappings***  
*F.T. Hioe, Dept. of Physics* **\$60,000**

This research program undertakes the following studies: (1) the newly discovered theory of multilevel adiabatic following will be extended to the study of selective multistep photoionization; (2) experiments will be suggested for observing multiphoton echoes and for understanding multiphoton relaxations; (3) a more complete theory of Landau-Zener effect at avoided crossings for multilevel systems will be formulated in relation to the optimum rate for accomplishing population inversion; and (4) multiple pulse propagation and the possibility of observing self-steepening or optical shocks will be explored.

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

**276. *X-Ray Emission in Heavy-ion Collisions***  
*R.L. Watson, Dept. of Chemistry* **\$68,900**

High resolution x-ray spectral measurements are being performed for the purpose of investigating: (1) rapid electron transfer in light elements following multiple ionization by fast heavy-ion impact; (2) excitation and x-ray emission from np states of fast heavy ions in gaseous and solid media; and (3) alignment of P states in ion-atom collisions. Spectra are obtained using a variety of beams, ranging from protons to argon ions provided by the Texas A&M variable energy cyclotron. The objectives of these experiments are to obtain a basic understanding of the processes responsible for chemical effects on x-ray satellite and hypersatellite structure, and to characterize solid state influences on x-ray emission from few-electron heavy ions, including alignment and possible coherence effects.

**University of Arkansas**  
**Fayetteville, Arkansas 72701**

**277. *Theoretical Study of Electron Capture in Ion-Atom Collisions***  
*M. Lieber, F.T. Chan, Dept. of Physics* **\$42,000**

Electron capture processes in ion-atom and ion-ion collisions (e.g.,  $A^+ + B$  yields  $A + B^+$ ) are of importance to several areas of research, such as the controlled fusion energy program, astrophysics, and atmospheric phenomena. As a prototype of a rearrangement collision that is experimentally accessible, charge

exchange has been studied since the earliest days of quantum mechanics, but the difficulty of calculation has limited theoretical progress. Recent work has shown that eikonal techniques can be successfully applied to problems of this type, and have surprising power and simplicity. Calculations are being performed on: (1) simultaneous capture of two electrons in  $He^{++}$  collisions with neutral atoms; (2) the connection between the eikonal approximation and asymptotic behavior of the wave function; and (3) the effect of Stark-mixing of energy levels on electron capture cross sections for capture into a subshell. We have recently turned our attention to multiphoton processes, which are of considerable interest both in terms of basic theory and in various practical applications. Previous theoretical work reported so far on absorption and ionization processes has involved only a single light beam. We plan to generalize the analysis of the two-photon process to the case of two incident light beams having arbitrary direction and polarization.

**University of Chicago**  
**Chicago, Illinois 60637**

**278. *Basic Studies of Atomic Dynamics***  
*U. Fano, James Franck Institute* **\$75,000**

This project aims at describing and predicting the correlations and the energy transfers among the variables of atomic and molecular systems. The observed but paradoxical stability of resonant states that are localized on top of potential barriers, rather than on valley bottoms, seems to have been eventually understood. It derives from a general property of light or particle beams focused about a symmetry axis or plane. Whichever action produces the focusing also confines the associated transverse wave, causing it to acquire a discrete stable spectrum. This concept is being developed into a semianalytic description of a WKB wave function with some channel components propagating on top of the barrier and others in the valleys. The initial application will construct the theory of the quasi-Landau resonances of Rydberg spectra in a magnetic field, but it should bear on all atomic and molecular reactions. Other current research on novel aspects of electron mechanics is progressing regularly.

**University of Colorado**  
**Boulder, Colorado 80309**

**279. *Spectroscopic Diagnostics of Electron-Atom Collisions***  
*A.C. Gallagher, Joint Institute for Laboratory Astrophysics* **\$78,000**

An experiment has been designed and construction has been initiated to measure cross sections for electron excitation of metal atoms. The experiment is designed to yield differential cross sections for spin changes as a function of electron scattering angle. The experimental plan utilizes 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.

**280. Near-Resonant Absorption By Atoms in Intense Fluctuating Fields**  
S.J. Smith, Joint Institute for Laboratory Astrophysics **\$56,700**

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 frequency 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. The role of fluctuations in nonlinear atomic absorption is measured in the two-photon  $3^2S-5^2S$  transition in sodium, in a Doppler-free configuration, and also in 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 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).

**University of Georgia**  
Athens, Georgia 30605

**281. Quantum Mechanical Studies of Heavy Ion Scattering Processes**  
T.G. Heil, Dept. of Physics and Astronomy **\$54,000**

This research project concentrates on low to intermediate energy 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 being studied in detail. Angular distributions are being calculated and interpreted for charge transfer reactions and other low energy heavy ion processes. These may prove to be a sensitive probe of the dynamics of low energy many-body collisions. Charge transfer processes between hydrogen atoms and multiply charged ions by both radiative and non-radiative mechanisms are also being studied. The charge transfer reactions  $[C^{2+} + H \rightarrow C^+ + H^+ + h\nu]$  and  $[Al^{3+} + H \rightarrow Al^{2+} + H^+]$  are being examined in detail.

**University of Kansas**  
Lawrence, Kansas 66045

**282. Theoretical Studies of Many-Body Processes in Atomic and Molecular Physics**  
S.-I. Chu, Dept. of Chemistry **\$64,000**

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) non-adiabatic theory for studying resonant IR 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; and (4) coupled dressed-quasimolecular-states approach for the study of laser-assisted charge-transfer reactions in slow ion-atom collisions.

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

**283. Low Energy Ion-Neutral Collisions**  
J.J. Leventhal, Dept. of Physics **\$70,000**

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 laser-induced processes of a type that could "turn on" certain chemical reactions. 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 are steps in the complicated sequences of reactions that collectively produce macroscopic effects, such as plasma formation, by coupling laser energy to gases or vapors. The possibility of modifying these macroscopic effects using laser-induced chemistry is also being investigated.

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

**284. Hyperspherical Coordinate Theory of Two-Electron Processes**  
J.H. Macek, A.F. Starace, Dept. of Physics and Astronomy **\$65,000**

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 He is studied using adiabatic hyperspherical coordinate initial and final state wavefunctions to compute the  $H^-$  form factors. The detached electron's angular distribution is highly sensitive to electron correlations. A pseudo-state method is developed to correct the gross inaccuracies of adiabatic hyperspherical wavefunctions at large radial distances. This procedure yields significantly improved  $^1S$  elastic phase shifts for electron scattering on atomic hydrogen. The Fock series expansion for two electron wavefunctions has been successfully implemented numerically. When matched to single channel adiabatic functions for some radius  $R_0$ , the Fock wavefunctions for He and  $H^-$  differ little (for  $0 < R < R_0$ ) from the adiabatic wavefunctions, at least for the lowest adiabatic channels. This confirms other recent theoretical results. The R-matrix for systems of coupled differential equations containing first derivative coupling matrix elements is found to be asymmetric. An alternative matrix (equal to the sum of the inverse R-matrix and the first derivative coupling matrix) is found to be symmetric. The Wannier threshold energy dependence of cross sections and angular distributions is derived quantum mechanically for the Coulomb breakup of three-particle systems with arbitrary angular momentum.

### University of New Mexico Albuquerque, New Mexico 87131

#### 285. *Atomic Physics With Relativistic Beams* H.C. Bryant, Dept. of Physics and Astronomy **\$95,000**

Exploitation of the relativistic kinematics of an 800 MeV H<sup>+</sup> beam at the Clinton P. Anderson Meson Physics Facility (LAMPF) at Los Alamos allows the observation, with very little background, of the one and two electron continua and embedded resonant structures. The H<sup>-</sup> system is being studied using Doppler-tuned laser probes and motional electric fields, which have so far ranged up to 7 MV/cm, far in excess of those possible using more conventional laboratory techniques. The behavior of the H<sup>-</sup> system as a function of both excitation energy and applied field is being carefully mapped out. Energy scale calibration is provided by excitation, with single photon absorption, of the Lyman series in an H<sup>0</sup> beam, derived from the H<sup>-</sup> beam by photodetachment. The studies of the <sup>1</sup>P resonant structures in H<sup>-</sup> near n=2, the shape and Feshbach resonances, and that of the 2 electron threshold region are proving to be exceptionally challenging to atomic physics theory, and more detailed measurements in these regions are planned.

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

#### 286. *Experimental Studies of Atomic Inner Shell Ionization Phenomena* S.M. Shafrath, Dept. of Physics and Astronomy **\$70,200**

This project is designed to study inner-shell vacancy production in ion-atom collisions, and subsequent decay via x-rays or Auger electrons. A position sensitive parallel plate electron spectrometer has been developed, and used to study metastable Auger electron emitting ion beams. A new design for high resolution projectile electron spectroscopy is in progress. Primary emphasis at this time is on experiments relating to dielectronic recombination. In a typical experiment, beams of fast, highly stripped ions, such as Si<sup>11+</sup> produced by the TUNL FN tandem Van de Graaff accelerator, are directed to interact with a helium gas target. The charge state of the projectile ion is then analyzed by means of an array of four parallel plate avalanche detectors. K-shell x-rays, which are detected with a Si(Li) detector in coincidence with ions that have captured or lost one or two electrons, are recorded. The charge transfer cross sections (i.e., electron capture and loss probabilities) are also measured directly, as are prompt and metastable K x-ray yields, K vacancy sharing cross sections, and radiative electron capture (REC). Each of these quantities is then compared with theory.

### University of Oklahoma Norman, Oklahoma 73019

#### 287. *Experimental and Theoretical Study of Very Low Inelastic Processes in Electron-molecule Collisions* M.A. Morrison, Dept. of Physics and Astronomy **\$27,000** (6 mo.)

The research project involves a comprehensive theoretical and experimental study of very-low-energy electron-impact excita-

tion of molecules. This research is directed at determining reliable cross sections for molecules of basic scientific interest and of relevance to technological applications such as advanced energy programs. The project seeks to resolve significant discrepancies that exist among the results of various experimental and theoretical investigations of near-threshold excitation of molecules by low-energy electrons, and to develop a deeper understanding of the physics of this important collision process. In the experimental part of the program absolute differential cross sections for low-energy, electron-impact excitation of these molecules shall be measured using a crossed-beam time-of-flight (TOF) apparatus which is especially suited to low-energy collision studies. The theoretical work entails carrying out accurate *ab initio* calculations of cross sections for vibrational and rotational excitation, and developing new methodologies for handling collisions with large complex molecular targets in the near-threshold energy regime.

### University of Rochester Rochester, New York 14627

#### 288. *Nonlinear Optics With Broad-Band Lasers* M.G. Raymer, Institute of Optics **\$70,000**

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 broad-band lasers are used to pump stimulated Raman amplification, and coherent anti-Stokes Raman scattering in hydrogen gas. Intensity and field cross-correlations which develop between pump and probe laser beams in these processes are being observed, using an intensity cross-correlator and a nonlinear interferometer based on the interference of beams produced at the sum-frequency of the two beams of interest.

### University of Tennessee Knoxville, Tennessee 37996-1200

#### 289. *Production and Destruction of Metastable Negative Ions* D.J. Pegg, Dept. of Physics **\$44,400**

This research project is designed to investigate the production and destruction of metastable negative atomic ions. In particular we begin our measurements on Ca<sup>-</sup>, where the 4s4p<sup>2</sup> <sup>4</sup>P state is theoretically predicted to be bound and metastable against allowed radiative and autodetachment decay mechanisms. Our source of negative ions is a fast moving beam, and we plan to use electron spectroscopic techniques to study the energy of electrons detached in flight by the processes of autodetachment, collisional detachment, and photodetachment.

### University of Texas Austin, Texas 78712

#### 290. *Kinetic Studies Following State Selective Laser Excitation* J.W. Keto, Dept. of Physics **\$74,000**

Electronic energy transfer from xenon atoms and excimers is studied following selective excitation by multiphoton laser excitation. Reactions at higher pressures where termolecular processes are observed are being emphasized. Initial experiments are studying radiative lifetimes and quenching of  $5p^66p$  xenon atoms in collisions with xenon and other rare gases. Accurate potential curves for xenon excimers are obtained by comparison of two-photon spectra with line broadening theories. Comparisons are made over a broad range of temperatures and pressures. Collisional deactivation rates are being measured. These rates are found to be dependent upon laser frequency. Atoms which absorb in the red wing of an absorption are excited as collision pairs at a unique inter-nuclear separation; hence, the laser prepares the reactant selectively on the collision surface. Experiments studying laser controlled reactive transfer are planned.

**University of Toledo**  
Toledo, Ohio 43606

291. *Semiempirical Studies of Atomic Structure*  
L.J. Curtis, Dept. of Physics & Astronomy **\$55,000**  
(24 mo.)

The structure and properties of very heavy and very highly ionized atoms are being studied through experimental measurements utilizing fast ion beam excitation, and through the identification and exploitation of regularities in the data base using precise empirical parametrizations. The use of spectroscopic line intensities to determine thermonuclear plasma temperatures and densities requires laboratory observation and analysis of these systems. The spectroscopic accuracies required are difficult to achieve by purely *ab initio* theoretical methods for many complex electron systems in this highly relativistic regime. Through the acquisition and systemization of experimental data, regularities and linearities are being utilized to predict a wide variety of atomic structure properties, which are subsequently tested experimentally. Recently, special emphasis has been given to the prediction of wavelengths and transition probabilities for metastable states in highly ionized atoms that decay by magnetic dipole, electric quadrupole, or spin-mixing processes, which are observed in Tokamak spectra.

**Vanderbilt University**  
Nashville, Tennessee 37235

292. *Theoretical Studies of Atomic Transitions*  
C. Froese Fischer, Dept. of Computer Science **\$82,000**

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 wavefunction, optionally corrected for relativistic effects in the Breit-Pauli approximation. Transitions of current interest are the forbidden transitions which may be important in astrophysics for the electron density, or which have been observed in Tokamak plasmas. Also of interest are the transitions between the doubly excited states of Ca 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 which may be characterized as bound-continuum transitions.

**Western Michigan University**  
Kalamazoo, Michigan 49008

293. *Correlated Charge Changing Interactions and K X-Ray Emission in Ion-Atom Collisions*  
E.M. Bernstein, J.A. Tanis, Dept. of Physics **\$60,000**

An experimental program to probe fundamental interactions in ion-atom collisions is being conducted. Individual inner-shell processes of excitation, ionization, and charge transfer are investigated for highly charged ions ( $12 \geq Z \geq 26$ ) incident on gas targets under single collision conditions. Cross sections for the various processes are measured for a range of projectile velocities (0.5 MeV/amu to about 8.0 MeV/amu) and incident charge states for several projectile and target species. Experimentally, this work is carried out by measuring coincidences between x rays (from the projectile and/or the target) and the outgoing projectile charge state of interest. Specific topics being investigated are: (1) resonant-transfer-and-excitation and associated processes; (2) excitation and ionization of projectiles and targets; and (3) electron capture to excited states ( $n \leq 2$ ) for hydrogenlike and bare projectiles. In addition, total cross sections for electron capture and loss are obtained. These results, when taken together, provide a rather complete picture of the collision dynamics for the projectile-target combinations investigated.

**Chemical Energy**

**Brigham Young University**  
Provo, Utah 84602

294. *Metal Support Interactions: Their Effects On Catalytic Properties of Cobalt*  
C.H. Bartholomew, Dept. of Chemical Engineering **\$71,800**

Metal-support interactions and their effects on adsorption and activity/selectivity properties of cobalt are being investigated. The objectives of this study are: (1) to determine the effects of cobalt-support interactions on dispersion, oxidation state, and adsorption properties of cobalt; (2) to correlate the catalytic properties for hydrocarbon synthesis on cobalt with dispersion, oxidation state, and CO and H<sub>2</sub> adsorption properties; and (3) to measure directly the extent of interaction of various supports with iron and cobalt using Moessbauer Spectroscopy. The work features a comprehensive, quantitative experimental investigation of Co on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, MgO, and carbon supports including careful characterization of the physical and chemical, bulk and surface properties of each catalyst with BET, H<sub>2</sub> and CO chemisorptions, XRD, TEM, TPD, and TPR measurements. Recent results provide evidence that dispersion and support significantly influence adsorption and CO hydrogenation activity/selectivity properties of cobalt.

**California Institute of Technology**  
Pasadena, California 91125

**295. Organometallic Catalysts and Analogs For CO Reduction and Carbon-Carbon Bond Cleavage Reactions**  
R.H. Grubbs, Dept. of Chemistry **\$107,000**

The research is concerned with the activation and reduction of carbon monoxide. Group VI-B intramolecular metalloesters are synthesized from cationic transition-metal(II) carbonyl complexes, employing intramolecular nucleophiles. Spectroscopic and x-ray crystallographic evidence confirm 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 configuration for intramolecular nucleophilic attack is being investigated. One-electron electrochemical oxidation of an arene chromium carbonyl complex results in the rapid substitution of the carbonyl ligands by added phosphines or solvent. The intermediate was identified. 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 binuclear complexes which show a wide range of reactivities and structures.

**Colorado State University**  
Fort Collins, Colorado 80523

**296. Chemically Modified Electrodes and Related Solution Chemistry**  
C.M. Elliott, Dept. of Chemistry **\$70,000**

New chemically modified electrodes and related solution chemistry are under study in this research. The goal is to alter the kinetics of electrode reactions in a useful way. Of primary interest is the catalysis of various kinetically inert small molecules that are of economic interest; in particular, the respective four electron and six electron reductions of dioxygen and dinitrogen. Different synthetic procedures appropriate for each of the materials under study are being investigated in order to chemically bind the potential catalyst to the surfaces of bulk electrode materials. Our primary emphasis is the development of polymer coated electrodes containing the potential catalyst and/or other electroactive materials. Several such electrodes have been prepared and are under active investigation. A number of novel metalloporphyrin compounds have been prepared, and their catalytic activity is presently under investigation both in solution and polymer bound. The primary methods of investigation of these surfaces are electrochemical, including such techniques as chronoamperometry, cyclic voltammetry, and the rotated disk electrode technique.

**297. Diosmacycloalkanes As Models For the Formation of Hydrocarbons From Surface Methylene**  
J.R. Norton, Dept. of Chemistry **\$52,000**  
(7 mo.)

This project develops an efficient general synthesis of diosmacycloalkanes. The project will then 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

ear systems. The project will also see if hydrocarbon C-H bonds can be activated by  $\text{Os}(\text{CO})_4$  or any other species generated photochemically from  $\text{Os}(\text{CO})_5$ .

**298. Reactions of Alkyl Palladium and Platinum Dimers: Mechanisms of Dinuclear Elimination**  
J.K. Stille, Dept. of Chemistry **\$68,000**

Metal clusters can serve as models for metal surfaces in catalysis, and because the cluster is well defined and amenable to study by the methods and techniques available to homogeneous systems, the reactions on clusters can be studied in detail. Thus, a knowledge of the mechanisms of reactions that occur on clusters can provide a better understanding of heterogeneously catalyzed reactions, and help in developing new heterogeneous catalysts. The synthesis of dinuclear platinum, palladium, and rhodium complexes containing organic groups on adjacent bonded metals, and the reactions of these complexes, particularly the 1,2-reductive elimination, rearrangement, oligomerization, and insertion reactions are being carried out. Elucidation of the mechanism(s) of these reactions should provide a better understanding of how coupling, oligomerization, and isomerization reactions of hydrocarbons take place on metal surfaces.

**Harvard University**  
Cambridge, Massachusetts 02138

**299. Model Studies of Hydrodesulfurization and Hydrodenitrogenation On Sulfided Molybdenum Surfaces**  
C.M. Friend, Dept. of Chemistry **\$49,900**

This program is directed toward the study of hydrodesulfurization and hydrodenitrogenation reactions on sulfided molybdenum surfaces. Model studies on well-characterized sulfided single-crystal molybdenum surfaces will be performed, both in ultra-high vacuum and at high pressures ( $\geq 1$  atm). These complementary experiments will help delineate key factors that control C-S and C-N bond activation on sulfided molybdenum surfaces. A range of experimental spectroscopic and chemical techniques will be utilized in ultra-high vacuum in order to identify and characterize reaction intermediates and model catalyst surfaces prior and subsequent to the high pressure reaction. Reaction product distributions at high pressure will be monitored by gas chromatography and/or mass spectrometry of trapped products.

**Indiana University**  
Bloomington, Indiana 47405

**300. Metal Alkoxides—Models For Metal Oxides**  
M.H. Chisholm, Dept. of Chemistry **\$146,500**  
(24 mo.)

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 reports during the 1983-1984 period are: (1) the cleavage of C=O to carbido and oxo tungsten alkoxide clusters; (2) the coupling, co-coupling, and sometimes metathesis-like reactions ( $M = W$ )

between C triple bond C, C triple bond N and M triple bond M bonds in  $M_2(OR)_6$  compounds; (3) unusual  $\beta$ -hydrogen effects in dinuclear alkyl-alkoxides 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  $W_2(\mu-H)(OR)_8^-$  which have been isolated as sodium salts.

**301. Radical Chain and Rearrangement Reactions in Coal Liquefaction**

*J.J. Gajewski, K.E. Gilbert, Dept. of Chemistry* **\$71,000**

This project focuses on providing fundamental data for the thermal reactions of aromatic compounds that may serve as a basis for understanding coal liquefaction. It has been shown that 1,3-diarylhydrocarbons and ethers decompose by free radical chain processes in the temperature range of 310 to 390°C. Some of these species will react with lower temperature free radical initiators, and the kinetics and the thermodynamics of these reactions have been studied. Hindered phenols will inhibit radical chain reactions up to 200°C. We have also found that phenyl substituted tetralins cleave to smaller molecules via a complex series of radical rearrangements and phenyl shifts. Also, *p*-isotoluene and benzo-*p*-isotoluene, putative intermediates in the concerted retro-ene decomposition of 1,3-diphenylpropane, undergo thermal reactions with second order kinetics to give non-ene dimers and polymers respectively. Finally, alkenes have been found to oligomerize in competition with reduction to alkanes in hydrogen donor solvents.

**Indiana University-Purdue University at Indianapolis**  
Indianapolis, Indiana 46223

**302. Studies of Metal-Ammonia Interactions With Aromatic Substrates**

*P.W. Rabideau, Dept. of Chemistry* **\$54,000**

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. This research is aimed at a better understanding of the fundamental nature of this reaction, using aromatic and polynuclear aromatics as model compounds. The intermediates in these reactions are monoanions, radical anions, and dianions, and efforts to study them involve direct and indirect methods. Direct studies include proton and carbon NMR with monoanions in liquid ammonia, whereas indirect studies involve determination of protonation sites (regioselectivity), and stereochemical outcome of alkylation. The conformational analysis of the reduced products (partially unsaturated six membered rings) is also being considered experimentally with proton and carbon NMR, as well as theoretically with force field calculations.

**Lehigh University**  
Bethlehem, Pennsylvania 18015

**303. Mechanisms and Controlling Characteristics of the Catalytic Oxidation of Methane**

*K. Klier, G.W. Simmons, R.G. Herman, J.E. Sturm, Dept. of Chemistry* **\$210,000**  
(24 mo.)

The objective of this project is to investigate the role of metal and oxide catalysts on the selectivity of product composition in partial and full oxidations of methane. Studies of both the gas phase free radical pathways and the surface catalyzed reactions, as well as the interplay of the two, are incorporated in this project, using modern tools of spectroscopic characterization of gas phase intermediates (EPR, optical) and of surface intermediates (Auger/ESCA/LEED/EELS). The gas phase and surface reactions occurring during partial oxidation of methane are being analyzed separately, and the project is divided into four activities: (1) trapping, detecting, and identifying of free radicals; (2) electron spectroscopy of surface intermediates, and Auger/ESCA/LEED/TPD studies of halogen-treated palladium crystal surfaces; (3) kinetic and mechanistic study of the catalyzed combustion of methane; and (4) effects of nitric oxide.

**Marquette University**  
Milwaukee, Wisconsin 53233

**304. Polymer-Based Catalysts**  
*S.L. Regen, Dept. of Chemistry* **\$60,900**

This research is aimed at developing highly active and stable polymeric catalysts for use in aqueous/liquid organic two phase and aqueous/resin/liquid organic three phase reactions. Current effort is focusing on poly(ethylene glycols) and poly(ethylene glycol)-grafted copolymers as catalysts for promoting dehydrohalogenation, alkylation, and saponification processes. Preliminary results indicate that significantly improved synthetic procedures are possible based on such catalysts, which should be amenable for a variety of laboratory as well as industrial applications.

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

**305. Reduction of Carbon Monoxide**  
*R.R. Schrock, Dept. of Chemistry* **\$215,000**  
(24 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. The approach is to discover how earlier transition metal hydride complexes can take part in unique reactions not possible with the later transition metals i.e., what new principles of catalytic reduction of carbon monoxide remain to be discovered. The project involves the synthesis of new transition metal hydrido complexes and a detailed study of how they react with carbon monoxide to give a  $\mu$ -hydrido  $\mu$ -formyl species. Analogous reactions employing metals which are less oxophilic are being sought. At present, we are investigating some novel tungsten hydrido clusters and complexes containing linked cyclopentadienyl ligands, including a late/early transition metal combination. The late/early transition metal complex is being tested for activity under typical syngas conditions.

**National Bureau of Standards  
Washington, District of Columbia 20234**

**306. Structure and Reactivity of Chemisorbed Species and Reaction Intermediates**  
*T.E. Madey, R.D. Kelley, Division of Surface Sciences* **\$126,000**

This project addresses the structure and reactivity of adsorbed molecules both on single crystal catalysts and on high area catalysts using a variety of experimental methods. It involves four areas of research which have a common theme, the investigation of surface processes related to catalytic chemistry: (1) the role of catalyst promoters and poisons (Na,S,O) in inducing new surface structures in molecular complexes adsorbed on metal and oxide surfaces is being studied, using the electron stimulated desorption ion angular distribution (ESDIAD) method; (2) vibrational spectroscopy of the adsorption, decomposition, and reaction kinetics of CO, O<sub>2</sub>, H<sub>2</sub>O and NH<sub>3</sub> on single crystal metal and oxide surfaces is being studied, using high resolution electron energy loss spectroscopy (EELS); (3) neutron inelastic scattering (NIS) is being used to characterize the vibrations of surface species on Raney Ni and Pt-black catalysts, and the utility of NIS as an *in situ* surface vibrational probe of CO hydrogenation under reaction conditions is being pursued; and (4) hydrogenation and hydrogenolysis reactions over single crystal catalysts (tungsten, tungsten carbide, Cu/Ni alloys, and small particles supported on oxide surfaces) are under investigation.

**Northwestern University  
Evanston, Illinois 60201**

**307. Solid State, Surface, and Catalytic Studies of Oxides**  
*H.H. Kung, Dept. of Chemical Engineering* **\$88,600**

The purpose of this project is to elucidate the interrelation among the solid state, surface, and catalytic properties of oxides. Current emphasis is on the effect of crystalline size and surface atomic structure in surface chemistry and catalysis. In the former, Fe<sub>2</sub>O<sub>3</sub> catalysts of average crystallite sizes ranging from 2.5 to over 100 nm were prepared. Moessbauer, x-ray, and magnetization measurements indicated the presence of only  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. When used as catalysts for butene oxidation, the selectivity for butadiene was found to decrease from about 80% to less than 40% with increasing crystallite size. In the study of surface atomic structure effect, single crystal planes of (0001), (10 $\bar{1}$ 0), (40 $\bar{4}$ 1), and (50 $\bar{5}$ 1) of ZnO were used in the decomposition of methanol, formaldehyde, and formic acid. The product distributions on (10 $\bar{1}$ 0), (40 $\bar{4}$ 1), and (50 $\bar{5}$ 1) were the same, but the decomposition activity increased with step density. The primary reaction is the oxidation to formate which decomposed into CO, CO<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>O. On the (0001) surface, in addition to oxidation, a dehydrogenation pathway also exists to yield formaldehyde, H<sub>2</sub>, and CO from methanol.

**308. Supported f-Element Organometallic Complexes: Surface Chemistry and Catalysis**  
*T.J. Marks, R.L. Burwell, Jr., Dept. of Chemistry* **\$71,000**

This project involves a study of the surface chemistry and catalytic activity of organoactinide complexes deposited on oxide supports. Two complexes, M=Th, U in M[(CH<sub>3</sub>)<sub>5</sub>C<sub>5</sub>]<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>

had been found to give very rapid hydrogenation of propylene at -63°C, and polymerization of ethylene at 25°C. Th[(CH<sub>3</sub>)<sub>5</sub>C<sub>5</sub>]<sub>2</sub>H<sub>2</sub> dimer and Th[(CH<sub>3</sub>)<sub>5</sub>C<sub>5</sub>](benzyl)<sub>3</sub> have now been found to exhibit similar or higher activity for hydrogenation, but U[(CH<sub>3</sub>)<sub>5</sub>C<sub>5</sub>]<sub>2</sub>(CH<sub>3</sub>)Cl has only 5% as much activity. Poisoning experiments with CO indicate that only a few percent of the U or Th atoms become active sites for these reactions. During activation, a fraction of U[(CH<sub>3</sub>)<sub>5</sub>C<sub>5</sub>]<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub> loses methane to form the alkylidene U=CH<sub>2</sub>, probably stabilized by interaction with surface Al. A number of the adsorbed species have been directly observed by high resolution solid state nmr techniques.

**309. Chemical Interactions in Bimetal/Zeolite Catalysts**  
*W.M.H. Sachtler, Dept. of Chemistry* **\$82,600**

For zeolite supported metals, the catalytic potential of bi- or multi-metal catalysts is still basically unexplored. An essential prerequisite for the development of this field is to enhance the interaction of transition metals with the zeolite framework, in order to impede migration of metal atoms to the outer surface, where they agglomerate to large particles. The primary objective of this research is, therefore, to improve the interaction between transition metals and zeolites. The ability of ions with unfilled d- or f-orbitals of appropriate energy to act as "anchors" for reduced transition metals is investigated. The dispersion of metals (e.g., Pt or Rh on zeolites doped with Fe<sup>3+</sup> or Cr<sup>3+</sup>) is studied. Claims in the literature that such ions enhance the dispersion of Pt are verified. ESR or EXAFS will be used to identify the valency of the ions after reduction and the interaction of paramagnetic ions with metal atoms. The catalytic performance of the bimetal/zeolite combinations is studied, using the hydroisomerization of methyl cyclopentane as an allegedly structure-sensitive test reaction, and compared with the performance of the monometal/zeolite reference systems. While attention is mainly focused on effects due to enhanced dispersion maintenance, we also look for indications that catalyst selectivities and/or activities are affected, as found previously for bimetal catalysts on other supports.

**310. Structure and Chemistry of the Interaction of Organometallics With Surfaces**  
*D.F. Shriver, Dept. of Chemistry* **\$94,500**

The objective of this research is to characterize organometallics attached to surfaces. The primary techniques include quantitative analysis of gases evolved upon interaction of the organometallic with the surface, Fourier transform infrared spectroscopy, Raman spectroscopy, and extended x-ray absorption fine structure. Initial studies will center on metal carbonyls attached to the metal oxide surfaces. Parallel studies will be performed on molecular compounds which simulate the proposed surface species. Catalytic activity of some of the surface organometallics will be investigated.

**Owens-Illinois, Inc.  
Toledo, Ohio 43666**

**311. Investigation of the Nature of Semisynthetic Esterases**

*M.H. Keyes, Dept. of  
Biotechnology*

**\$69,400**

This research project is designed to study the nature of semisynthetic esterases, generated from nonesterase proteins, by means of conformational modifications induced by inhibitors of natural esterases. Two esterases are being generated from bovine pancreatic ribonuclease, using indolepropionic acid as the modifier, after perturbing the protein under acid pH and cross-linking with glutaraldehyde. The esterase activity is assayed using tryptophan ethyl ester as substrate and measuring the ethanol produced. The two esterases are distinguished by their distinct pH optima, substrate specificity, and inhibition by tryptophan. After separation by ammonium sulfate precipitation, further purification of the esterases is being accomplished by gel filtration. The specificity of the esterases is being investigated using various esters, and amide substrates. Kinetic studies on the most appropriate substrates are being done.

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

**312. Mechanistic Studies of Carbon Monoxide Reduction**

*G.L. Geoffroy, Dept. of Chemistry* **\$78,000**

Mechanistic schemes for the metal surface catalyzed reduction of carbon monoxide to methanol and to hydrocarbons have been proposed, and the feasibility of these mechanisms is being tested by preparing and studying the chemistry of metal clusters which resemble the proposed surface intermediates. Initial focus was on the preparation and reactivity studies of cluster complexes bearing formyl and acyl substituent groups. The stepwise reduction of CO to CH<sub>4</sub> on an Os<sub>3</sub> cluster via a formyl intermediate was observed. More recently it has been found that Os<sub>3</sub>(CO)<sub>11</sub>(μ-CH<sub>2</sub>), an isolatable intermediate in the preceding transformation, reacts readily with CO to yield the first ketene substituted cluster, Os<sub>3</sub>(CO)<sub>12</sub>(H<sup>2</sup>(C,C),μ<sub>2</sub>-CH<sub>2</sub>CO). This species has been characterized spectroscopically and by a single crystal x-ray diffraction study; its chemistry is now being explored in detail. A series of mixed-metal dinuclear complexes have been synthesized, and their CO/H<sub>2</sub> reactivity is being examined. Focus is on dinuclear complexes containing one early and one late transition metal and held together by bridging μ-PR<sub>2</sub> groups.

**313. The Nature of the Contribution of the Polymers of Cell Walls of the Higher Plants to Coal Formation**

*P.H. Given, Coal Research Section* **\$55,000**

The objective of this project is to identify in peats the chemically altered forms of the plant polymers that constitute the input to coalification. Cores from four sites in the Florida Everglades and Okefenokee swamp have been obtained. About 30 to 50% of the organic matter in all levels of a peat derived from the red mangrove consists mostly of tissue from the rootlets and secondary roots of the tree. Specimens of these organs hand-picked from the upper layers of the peat show strong carbohydrate character, judging from FTIR and <sup>13</sup>C nmr spectra, but are not purely cellulosic. Nevertheless, the abundant rootlets from +40 mesh sieved material has a pronounced aromatic character, which resembles but is not identical with lignin, apparently because the rootlet material is encrusted with brown amorphous

(humic?) substances. It has been found that oxidation with pertri fluoroacetic acid almost completely destroys cellulose but with lignin gives a good yield of a rather small number of simple polycarboxylic acids. The method has promise for the study of peats. In summary, the peat studied contains both carbohydrate- and lignin-related substances, but these are not identical with the natural polymers.

**314. Characterization of Active Sites and Their Role in Gas-carbon Reactions**

*R.G. Jenkins, P.L. Walker, F.J. Vastola, Dept. of Chemistry* **\$88,800**

This research project is concerned with measuring the concentration of active sites on carbons varying in crystallite size and orientation (all the way from microporous carbons of poor crystallinity to natural graphite flakes of high crystallinity), and relating this concentration to gasification rates. Previous work has shown that the steady state gasification rate at 0.1 MPa O<sub>2</sub> correlates with the total amount of surface oxide, and that CO can inhibit the steady state gasification rate. Current work is focused on characterizing the surface oxide formed during steady state gasification under varying conditions of temperature, pressure, and duration of reaction. The C-O<sub>2</sub> reaction is significantly catalyzed by Pt: e.g., the rate is about 400 times larger for 1% Pt deposited on a graphitized carbon black compared to the uncatalyzed case at 775 K and 0.1 MPa air. The reaction rates (673-773 K and 0.01 to 0.1 MPa O<sub>2</sub>) are found to depend on the amount of Pt on the sample. The Pt dispersions on various samples are being determined by an x-ray line broadening and O<sub>2</sub>-CO titrations at 298 K. The rate constants are found to be independent of average Pt dispersions.

**315. Transition Metal Catalyzed Transformations of Unsaturated Molecules**

*A. Sen, Dept. of Chemistry* **\$71,000**

The present research is concerned with the study of several novel homogeneous transition metal catalyzed reactions. A common feature of these catalytic processes is the use of relatively inexpensive small molecules (e.g., olefins and carbon monoxide) as building blocks in catalytic cycles to make more elaborate, larger molecules. The catalytic reactions currently under study are: (1) the stereospecific tail-to-tail dimerization of alkyl acrylates; and (2) the copolymerization and cooligomerization of carbon monoxide with olefins, dienes, and acetylenes. The latter transformations, under mild conditions, were discovered by us in the course of our previous studies. Since these catalytic processes are of considerable interest from a practical standpoint, we have undertaken a detailed study of their mechanism and scope. We expect to use the insight gained from such a study to tailor catalysts for higher specificity and/or milder reaction conditions.

**316. Metal-Support Interactions in Ni, Pd, and Pt Catalysts**

*M.A. Vannice, Dept. of Chemical Engineering* **\$81,500**

This research project is directed toward a better understanding of the chemistry involved in the creation of metal-support interactions in certain systems, which have been found to have pronounced effects on adsorption and catalytic behavior. This project involves a study of heats of adsorption and adsorption/desorption behavior for H<sub>2</sub>, CO and O<sub>2</sub> on Pt, Pd, and Ni, using

a modified differential scanning calorimeter and a thermal gravimetric analysis unit. Kinetic investigations are being made on the hydrogenation of carbon monoxide and aromatic hydrocarbons, beginning with benzene. Possible correlations between catalytic activity and adsorbate-metal bond strengths are being investigated. Recent results indicate that activity enhancement is due to additional active sites occurring in the metal-support interface region, and that surface bond strengths do not decrease on TiO<sub>2</sub>-supported Pt and Pd although adsorption decreases markedly. This multifaceted approach should provide a more complete explanation of both the much higher catalytic activities already found in certain reactions and the suppressed chemisorption which is observed after the SMSI state is induced.

**Purdue University**  
West Lafayette, Indiana 47907

**317. Reduction of Aromatic Compounds Derived From Coal By Calcium**  
*R.A. Benkeser, Dept. of Chemistry*      **\$60,000**

The versatility of the new reducing system consisting of calcium metal dissolved in a mixture of methylamine-ethylenediamine has been broadened considerably. By the simple expediency of adding an alcohol to the usual calcium-mixed amine system, it is now possible to reduce aromatic hydrocarbons which are abundant in coal to dihydro compounds (Birch-type products) rather than to tetrahydro products. Thus o-xylene can be reduced in high yield to 1,2-dimethyl-1,4-cyclohexadiene, m-xylene to 1,5-dimethyl-1,4-cyclohexadiene and p-xylene to 1,4-dimethyl-1,4-cyclohexadiene. The role played by the methylamine in these reductions is multifold. Its presence ensures that the calcium does not become coated with an insoluble substance during the course of the reduction. This coating often causes the reduction to stop and low yields of products result. This coating seems to be some type of a calcium amide. In many cases, the methylamine can be omitted and the reduction made to proceed very well in pure ethylenediamine provided a large excess of calcium is used. Another alternative which obviates the need for methylamine is to use a Hershberg stirrer and sand. The latter combination provides an abrasive action which prevents the calcium from becoming coated.

**Rensselaer Polytechnic Institute**  
Troy, New York 12181

**318. Homogeneous Carbon Monoxide Fixation**  
*A.R. Cutler, Dept. of Chemistry*      **\$185,000**  
(24 mo.)

Organometallic complexes containing C<sub>1</sub> alkoxycarbonyl and C<sub>2</sub> carboalkoxymethyl ligands derived from terminally bound CO are being synthesized in order to delineate those coordinate ligand reactions and their intermediates that are viable for CO hydrogenation. The metalloester FpCO<sub>2</sub>CH<sub>3</sub>, derived from FpCO<sup>+</sup> or from Fp<sub>2</sub>Mg/CO<sub>2</sub>, serves as the common template in converting either CO or CO<sub>2</sub> into the C<sub>1</sub> alkyl ligand on FpCH<sub>2</sub>OCH<sub>3</sub>; Fp = (H-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>. The activated ester FpC(OCH<sub>3</sub>)<sub>2</sub><sup>+</sup> thus adds hydride and gives its stable formylacetal FpCH<sub>2</sub>(OCH<sub>3</sub>)<sub>2</sub>, which subsequently affords the desired FpCH<sub>2</sub>OCH<sub>3</sub>. The metylidene salt FpCH<sub>2</sub><sup>+</sup> (generated from FpCH<sub>2</sub>OCH<sub>3</sub>) picks up exogeneous CO, ascertained by a <sup>13</sup>C

labeling study, and gives the stable (H<sup>2</sup>-C,C) ketene complex Fp(CH<sub>2</sub>CO)<sup>+</sup>PF<sub>6</sub><sup>-</sup>; this complex abstracts methoxide from methanol (or even FpCH<sub>2</sub>OMe) and provides the carbomethoxy methyl FpCH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>. This ketene complex, which effectively derives from two carbonyls, therefore serves as an efficient source of a C<sub>2</sub> alkyl ligand that is important in CO fixation studies.

**SRI International**  
Menlo Park, California 94025

**319. High Temperature Chemistry of Complex Vaporization/Decomposition Processes**  
*D.L. Hildenbrand, R.D. Brittain,*      **\$60,900**  
*K.H. Lau, Physical Sciences*  
Division

The objective of this program 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 by 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 primarily with metal sulfate and carbonate processes, with recent work on the sulfates of Cs, Rb, and Li, and carbonates of K and Cs. 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.

**320. Adsorption Thermodynamics and Surface Transport of Metal Catalysts Poisons**  
*H. Wise, Materials Research Lab.*      **\$76,500**

This research has for its objective a fundamental understanding of the binding energy of sulfur and halogen adatoms to metal surfaces in order to relate catalysts poisoning and reactivation to covalent bond formation. The experimental measurements involve studies of equilibrium adsorption and surface diffusion on single crystals of different orientations, and on highly dispersed metal catalysts. The techniques employed include classical studies of reversible adsorption at low surface coverages, temperature programmed desorption and surface reaction, Auger electron spectroscopy for diffusional transport, low energy electron diffraction for determination of surface coordination and reconstruction, and segregation experiments for study of the interaction of different CO-adsorbed surface species. At low surface coverage of sulfur significant variations in binding energy have been observed for different metals. Relative to Ni the sulfur adatoms are less strongly bound in the series Ni > Co > Ru > Fe > Ir > Cu > Pt. Typically the bonding of sulfur appears to involve the sp and d bands of the metals and the sulfur 3p orbitals, as observed by photoelectron spectroscopy. Theoretical correlations are in progress to relate the binding energy of sulfur to the electronic structure of the metal.

**Stanford University**  
Stanford, California 94305

- 321. Catalyzed Gasification of Carbon**  
*M. Boudart, Dept. of Chemical Engineering* **\$75,000**

Unsupported molybdenum carbide powders with high specific surface area and alumina supported highly dispersed molybdenum carbide clusters possess very high catalytic activity for the hydrogenolysis of n-butane. The surface of the powders normally contains polymeric carbon which must be removed by temperature programmed reduction with dihydrogen. These materials are currently investigated as new catalysts for CO-H<sub>2</sub> reactions.

- 322. Molecular Beam Studies of the Dynamics of Activated Adsorption of N<sub>2</sub> On W(110)**  
*R.J. Madix, Dept. of Chemical Engineering* **\$218,500**  
(24 mo. FY 83)

The activated adsorption of N<sub>2</sub> on W(110) was studied using molecular beams to achieve translational energies from 2 to 30 kcal/mol. The beams were formed in nozzles with and without helium seeding. For the lowest kinetic energy, the probability of dissociation upon collision was about 10<sup>-3</sup>, increasing to 2 x 10<sup>-1</sup> at energies above 20 kcal/mol. The dependence of the dissociation probability on nitrogen coverage suggested the process was direct in nature, not trapping dominated. The results show that adsorption is translationally activated, and that the reactive collision is not adequately described by a one-dimensional barrier. As the beam energy was increased, the apparent saturation coverage by nitrogen increased, producing an unusual desorption state above a nitrogen atom coverage of 2.5. Nitrogen desorbed autocatalytically from this state in a fashion observed previously for high concentrations of oxygen from Pt(100). The emergence of this state at higher surface coverages indicates that the state of nitrogen adsorbed on tungsten and other metals may be different from the state normally observed in low pressure studies. Additional measurements of the angular distribution of scattered dinitrogen indicated that the unreacted N<sub>2</sub> did not probe the potential energy surface for reaction. Angular profiles were observed which would be expected for quasi-elastic scattering. Similar experiments are in progress for CO<sub>2</sub> on Ni(100).

**Syracuse University**  
Syracuse, New York 13201

- 323. Metal-Support Interactions: The Effect of Catalyst Preparation On Catalytic Activity**  
*J.A. Schwarz, Dept. of Chemical Engineering & Material Sciences* **\$73,500**

That the catalytic properties of a dispersed metal are influenced by the composition of the support material and by subsequent reduction procedure is well known. Recent study suggests that the procedure by which a catalyst is prepared also influences its properties, but relatively little fundamental research on the phenomena has been reported in the literature. It is proposed that this project develop a scientific basis for design and control of catalyst systems by examining the relationship between catalyst preparation procedures and the activity, selectivity, and stability of the finished catalyst. Nickel dispersed on a series of silica-

alumina supports has been chosen as the prototype system because the amount and chemical properties of the nickel can be regulated by controlling the pH of the impregnating solution. The physicochemical properties of the prepared catalysts are determined by means of temperature programmed reduction, desorption, and reaction in conjunction with gravimetric and magnetization measurements.

**Texas A & M University**  
College Station, Texas 77843-3255

- 324. Catalysts and Mechanisms in Synthesis Reactions**  
*J.H. Lunsford, Dept. of Chemistry* **\$80,900**

A major part of this research project is devoted to understanding the structural and electronic factors which determine the catalytic properties of supported metals, such as palladium, for the formation of alcohols. Controlled modifications of the support, for example by the addition of lithium ions, can transform an inactive catalyst into one which rivals commercial catalysts for methanol synthesis activity. Infrared experiments, using CO as a probe molecule, are under way to determine the relative amounts of Pd(111) and Pd(100) planes which are exposed on the supported catalysts. Another aspect of the research involves a study of matrix-isolated gas phase radicals, which are produced on surfaces of catalytic importance. Recent work on magnesium oxide shows that surface defects which give rise to O<sup>-</sup> ions (V-type centers) are active for the generation of methyl radicals from methane. These centers are present only on oxygen-rich surfaces, which is surprising since magnesium oxide is normally considered to be a nonreducible oxide.

- 325. Catalytic Behaviors of Multi-valent Lanthanide Oxides**  
*M.P. Rosynek, Dept. of Chemistry* **\$131,200**  
(24 mo. FY83)

This research project involves a systematic investigation of the influence exerted by selected lanthanide oxide supports, principally those of La, Ce, Pr, and Eu on the catalytic behaviors of both well-dispersed (Pt, Rh) and poorly-dispersed (Fe, Co, Ni) transition metals, with a view toward identifying evidence for significant metal-support interactions. Supports being studied as a basis of comparison include silica, alumina, and titania. Catalytic behaviors of the various metals are being evaluated for appropriate diagnostic reactions (CO hydrogenation and paraffin hydrogenolysis/dehydrocyclization) as a function of conditions and support identity. These results are being correlated with those of accompanying characterization studies, involving infrared and x-ray photoelectron spectroscopies, transmission electron microscopy, and selective chemisorption measurements in an attempt to elucidate the nature and extent of metal-support interaction effects.

**University of California/Irvine**  
Irvine, California 92717

- 326. Synthesis, Chemistry, and Catalytic Activity of Lanthanide Metals in Unusual Oxidation States and Coordination Environments**

*W.J. Evans, Dept. of Chemistry*      **\$73,000**

The objective of this research project is to identify the special chemical properties of the lanthanide metals (14 heavy metals which are mined in California) and to exploit this unique chemistry to develop: (1) new materials of potential practical importance; (2) more efficient and more selective catalytic systems; and (3) new stoichiometric and catalytic reactions not presently possible with conventional catalysts. Our study of the chemistry of the lanthanide-carbon bond has led to the first molecules containing lanthanide-hydrogen bonds. These lanthanide hydrides catalytically activate molecular hydrogen, and we are studying the intermediates in this reaction to understand how to modify this reactivity in unusual ways. The reactions of the hydrides with nitriles, isocyanides, alkynes, and alkenes provide new, structurally unusual complexes whose chemistry is being examined. We are investigating the subtle factors which have major effects on the rates of several of the above classes of four-center reactions. We have developed an efficient conversion of bimetallic hydrides to structurally unique trimetallic tetrahydrides and mixed metal intermetallic tetrahydrides, which may be of interest with respect to hydrogen storage. We are studying the extension of this synthesis to larger polymetallic lanthanide polyhydrides.

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

**327. Metallocarboranes Structurally Engineered For the Reduction of Carbon Monoxide**  
*M.F. Hawthorne, Dept. of Chemistry*      **\$73,500**

This research program has been designed to develop and evaluate various metallocarboranes as homogeneous catalysts for the transformation of CO into useful chemical feedstocks. Emphasis has been placed on several areas of interest: (1) the evaluation of the activity of rhoda- and ruthenacarborane complexes as catalyst precursors for the water gas shift reaction; (2) the synthesis of heterobimetallic metallocarboranes which possess both early and late transition metal vertices for the study of metal-metal cooperativity in the reduction of CO; and (3) the preparation and screening of a series of rhodacarborane complexes as hydroformylation catalysts. The ability to synthetically engineer the structural and electronic properties of metallocarboranes has proven to be an indispensable tool. The catalyst precursors used in these studies have been shown to exhibit several novel structural features which include a structurally sensitive *cislo/exo nido* tautomerism, a key feature in the ability of these species to activate small molecules such as dihydrogen.

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

**328. Homogeneous Catalysis of the Water Gas Shift Reaction**  
*P.C. Ford, Dept. of Chemistry*      **\$71,000**

Research is directed (1) toward elucidating fundamental mechanisms key to catalytic cycles including the water gas shift reaction, and (2) toward developing new homogeneous catalysts for such reactions. Studies in progress include kinetic investigations of important steps such as the nucleophilic activation of carbon monoxide coordinated to metal centers by a variety of species

including the oxy anions  $\text{HO}^-$  and  $\text{CH}_3\text{O}^-$  ( $\text{M-CO} + \text{RO}^- \rightarrow \text{M-CO}_2\text{R}^-$ ), the decarboxylation of hydroxy carbonyl adducts ( $\text{M-CO}_2\text{H} \rightarrow \text{M-H} + \text{CO}_2$ ), the reductive elimination of  $\text{H}_2$  from metal hydrides ( $\text{M-H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{M} + \text{OH}$ ), and the substitution reactions of metal carbonyl complexes. Systems under investigation are largely drawn from those shown to have potential as homogeneous catalysts in the reactions of carbon monoxide. The elucidation of these mechanisms will provide guidelines 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.

**329. Reactions of Iron Atoms With Molecules in Low Temperature Matrices**  
*R.G. Pearson, P.H. Barrett, Dept. of Chemistry*      **\$65,100**

The goal of this project is to study the reactivity of metal atoms and small clusters, with molecules in low temperature matrices. Moessbauer and infrared spectroscopies are used to identify the reaction products. Reactions between Fe,  $\text{Fe}_2$ , and iron clusters, and low temperature matrix isolated molecules of  $\text{N}_2$ , NO,  $\text{SO}_2$ ,  $\text{CH}_2\text{N}_2$ , and other small molecules are under investigation. This investigation includes the search for bond cleaving reactions of HX and  $\text{CH}_3\text{X}$  molecules, and the study of  $\text{CH}_2$ , NH and O bound to iron atoms.

**University of Chicago**  
Chicago, Illinois 60637

**330. Reactions of Electrophilic Reagents With Bituminous Coals: The Chemistry of the Reaction Products**  
*L.M. Stock, James Franck Institute*      **\$82,600**

During the initial months of the project we have concentrated on the ruthenium(VIII) catalyzed oxidation of coal. The aromatic molecules are selectively oxidized in this process to yield simpler structures. The products derived from 20 representative molecules have been worked out and the products from a representative bituminous coal have been studied by mass spectrometry. In addition, a quantitative method based upon isotopic dilution techniques has been worked out and applied successfully for the determination of the methyl groups in coal. This information can be used to predict the quantity of methane expected during low severity pyrolyses. The electrophilic reactions of bituminous coals with mercury(II) and lead(IV) are under investigation. The plumbylation reaction of Illinois No. 6 coal yields a product which 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 material. This work should provide a more secure basis for the discussion of the role of hydroxyl groups on coal conversion and hence enable their greater control.

**University of Colorado**  
Boulder, Colorado 80309

**331. Studies of New Elimination Reactions of Metal Complexes**  
*M.R. Dubois, Dept. of Chemistry*      **\$55,600**

This project is investigating elimination and rearrangement reactions of alkyl substituents on  $\mu_2$ -sulfido ligands in dimers of the general types  $[\text{CpMoSSR}]_2^n$  and  $[\text{CpMo}(\text{SR})_2]_2^n$  ( $n=0,-1,-2$ ). It has been proposed that the sulfido ligands and metal ions may participate in these reactions to provide low-energy pathways for new reaction types. Altering the nature and charge of the bridging ligands in these complexes results in significant shifts in the observed reduction potentials. The reactivity of the sulfido ligands can be tuned in this way to interact with a range of electrophiles and nucleophiles. For example,  $[(\text{CpMo})_2\text{S}_2\text{CH}_2(\mu\text{SCH}_3)_\mu\text{S}]^-$  reacts with alkynes to form dimers with alkenyl thiolate ligands. This reaction may serve as a model for a pathway for alkyne reduction involving sulfur sites in metal sulfide catalysts. New dimeric complexes of vanadium, tungsten, rhenium, and iron with bridging sulfido ligands have also been synthesized and characterized. The sulfur ligands in some of the tungsten complexes appear to react readily with hydrogen despite the fact that they are in a different electronic and structural environment than the reactive ligands in the molybdenum systems. Vanadium dimers which are isostructural with the molybdenum complexes show no evidence for ligand reactivity.

**332. Promoter Modifications of Catalytic Activity and Selectivity**

*J.L. Falconer, Dept. of Chemical Engineering* **\$79,300**

The effect of alkali promoters on the activity and selectivity for CO hydrogenation is being studied on supported metal catalysts. Temperature-programmed desorption and reaction (TPD, TPR), steady-state reaction and x-ray photoelectron spectroscopy are being used. The support is shown to have a strong influence on the changes induced by the alkali promoter. On Ni/SiO<sub>2</sub> and Ni/TiO<sub>2</sub> large decreases in activity are seen; on Ni/Al<sub>2</sub>O<sub>3</sub> the activity does not change significantly, and on Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> the activity increases. The strong effect of the support was attributed to an interaction of the support with the promoter. Rate changes measured by temperature-programmed reaction and by steady-state kinetics are in good agreement. The decreased rates are attributed to decreased hydrogenation rates of carbon monoxide and of carbon, due to weakened hydrogen bonding. This results in large increases in olefin selectivity. The activity on Ni/SiO<sub>2</sub> decreased rapidly with potassium concentration. Preparation method and alkali salt used were shown to have little effect on the change in activity. On unpromoted Ni/Al<sub>2</sub>O<sub>3</sub> the presence of multiple reaction sites was observed and a model was developed for the reaction.

**University of Connecticut**  
**Storrs, Connecticut 06268**

**333. Highly Dispersed Metal Atoms in Zeolites**  
*S.L. Suib, Dept. of Chemistry* **\$50,900**

The purpose of this program is to understand ways of producing small particles of highly reduced metals in zeolites. Current emphasis is on the effect of microwave discharge methods for the synthesis of highly dispersed metal atoms in zeolite pores. The metals that we are working with are Fe, Co, and Ni. The microwave discharge procedure provides a general method to produce small metal particles on other supports such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, polymers, and TiO<sub>2</sub>. Characterization of these materials

involves Moessbauer spectroscopy, ferromagnetic resonance, x-ray powder diffraction, and surface analyses with Auger, x-ray photoelectron spectroscopy, ion scattering spectroscopy, and secondary ion mass spectroscopy. Superparamagnetic iron (0) and cobalt (0) clusters less than 20 Angstrom in size are prepared. Another aspect of this research involves use of these zeolites in Fischer-Tropsch and methanation reactions.

**University of Delaware**  
**Newark, Delaware 19716**

**334. A Surface Science Investigation of Potential Intermediates, Catalysts, and Promoters in the Synthesis of Higher Alcohols By Metals**  
*M.A. Barteau, Center for Catalytic Science and Technology, Dept. of Chemical Engr.* **\$72,900**

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 will examine the formation, stability, and reactivity of these intermediates on clean and modified surfaces of rhodium and palladium, in order to determine the properties of these metals that lead one (Rh) to be active for synthesis of higher alcohols. By studying the influence of inorganic surface promoters upon alkoxide reactivity, we will determine the ability of promoters to alter the intrinsic catalytic properties of these metals, and probe the importance of promoter electronegativity in the modification of surface reactivity. Various C<sub>1</sub>-C<sub>4</sub> alcohols will be used as probe molecules in order to determine (1) the effect of hydrocarbon chain length on alkoxide stability and reactivity, and (2) the influence of interactions between the surface and the alkoxide hydrocarbon chain upon alkoxide stability. In order to study the reactions of these molecules, including the identity and kinetics of formation of both gaseous products and surface intermediates, we will apply a battery of essential surface spectroscopic techniques, including TPD, HREELS, UPS, and XPS.

**University of Minnesota**  
**Minneapolis, Minnesota 55455**

**335. Photochemical Properties of Transition Metal-Arene Complexes**  
*K.R. Mann, Dept. of Chemistry* **\$133,900**  
**(24 mo.)**

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 photoassisted agents, and in the synthesis of novel organometallic complexes.

**University of Nebraska**  
**Lincoln, Nebraska 68588-0304**

**336. Studies On Unusually Reactive Metal Powders—Preparation of New Organic Compounds**  
R.D. Rieke, Dept. of Chemistry **\$63,300**

This research project is involved with the preparation and study of highly reactive metal powders prepared by the reduction of metal salts with alkali metals. Current studies are concentrating on nickel, cadmium, uranium, palladium, and platinum. The nickel powders have been found to react rapidly with benzylic halides, and the resulting organonickel complexes yield dibenzyl. Aryl halides react rapidly with the nickel powders to produce biaryl compounds in high yields. Benzylic halides react with the nickel powders in the presence of acylhalides to produce benzyl ketones in high yields. Reactions of ROCOCOCl and benzylic halides with nickel powders yield benzyl ketones. These reactions proceed with a wide variety of substituents on the phenyl ring of the benzylic halides. Highly reactive uranium has been prepared, and found to react with a variety of oxygen containing substrates, such as nitrobenzene to yield azo benzene. The chemistry of cadmium, platinum, and palladium is also under investigation.

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

**337. The Heats of Formation of Gas Phase Organo-Sulfur Molecules and Applications of  $^{17}\text{O}$  and  $^{33}\text{S}$  NMR to Structure Determinations**  
T. Baer, S.A. Evans, Jr., Dept. of Chemistry **\$70,200**

This program emphasizes photoionization and heteronuclear NMR techniques directed toward the determination of structures and energetics of organosulfur molecules. The  $\Delta H_f^\circ$  of the series:  $\text{RS}^\ominus$  [R =  $\text{CH}_3$ ,  $\text{CH}_3\text{CH}_2$ ,  $(\text{CH}_3)_2\text{CH}$ , and  $(\text{CH}_3)_3\text{C}$ ] are being measured. In addition, the  $\Delta H_f^\circ$  of various sulfonyl compounds are being determined by bomb calorimetry to make these substances amenable for photoionization studies. Chemical oxidation of sulfenyl sulfur (-S-) to sulfones (-SO<sub>2</sub>-) and particularly, to sulfonic acids (-SO<sub>3</sub>H) serves to "quench" the quadrupolar broadening effect. This allows for the 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  $^{33}\text{S}$  chemical shifts in aryl sulfones and sulfonic acids are being evaluated, as well as the possible use of magic-angle spinning techniques for determination of  $^{33}\text{S}$  shift parameters in the solid state.

**University of Pittsburgh**  
Pittsburgh, Pennsylvania 15261

**338. Carbide Ad-layer As Rate Controlling Factor in CO/H<sub>2</sub> Catalysis**  
P. Biloen, Dept. of Chemical and Petroleum Engineering **\$154,000**  
(24 mo. 1983 Funds)

The objective of this project is to assess the reactivity and abundance of reaction intermediates present at the surface of CO/H<sub>2</sub> converting catalysts during steady-state catalysis. The central question which is being addressed is to what extent carbonaceous side products control the abundance of reaction intermediates. In a typical experiment, the isotopic constitution of the feed is being changed abruptly (e.g.,  $^{12}\text{CO}/\text{H}_2 \rightarrow ^{13}\text{CO}/\text{H}_2$ ). This

leads to a transient phenomenon: the displacement of  $^{12}\text{C}$  by  $^{13}\text{C}$ , 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  $^{12}\text{CO}$  and  $^{13}\text{CO}$  exhibiting essentially identical reactivity, the steady-state of the system is essentially not affected by the isotopic switch. In the present setup, the rate of isotopic substitution in product is being monitored by on-line mass spectrometry. Under construction is a setup to combine this with an *in situ* IR monitored rate of isotopic substitution in the reactive ad-layer.

**339. Studies of Supported Metal Catalysts**  
D.M. Hercules, Dept. of Chemistry **\$85,900**

We have advanced the adaptation of spectroscopic techniques for studying catalytic surfaces demonstrating the utility of ESCA, ISS, and LRS. LRS gives structural information about bulk phases, whereas ESCA gives information about dispersed phases. We have demonstrated a correlation between ESCA, EXAFS, and PAS measurements, giving information about site symmetry of transition metals on catalysts. We have shown a correlation between reducibility of catalytic species measured by ESCA and the same quantity measured classically. We have characterized Ni species on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> when the preparation method and Ni content of the catalysts are varied. We have determined the nature of Ni species on TiO<sub>2</sub>, ZrO<sub>2</sub>, and ThO<sub>2</sub> surfaces and their reducibility. We have studied the nature of Co species on Al<sub>2</sub>O<sub>3</sub>, and how they are affected by Mo or Zn, or by sulfiding. We have determined how Mo species on supported catalysts are affected by reducing or sulfiding, by the presence of Co, Ni, Zn, or by the nature of the support (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>). We have studied the effect of Mo impregnation pH on the nature and dispersion of Mo species, and the catalyst hydrodesulfurization activity. For tungsten on alumina, the catalyst W species differ from Mo for the same support; W species on alumina are affected by reducing, sulfiding, or by the presence of Ni.

**340. Infrared Studies of Influence of Alkali Metals On C-O Bond in Chemisorbed Carbon Monoxide**  
J.T. Yates, Dept. of Chemistry **\$136,100**

This research project is designed to probe the interaction of adsorbed alkali metals with adsorbed carbon monoxide on transition metal single crystal surfaces. Information obtained by reflection IR spectroscopy, x-ray, photoelectron spectroscopy, and temperature programmed desorption will yield models of the interaction, and deeper understanding of the alkali promotion effects observed in catalytic chemistry on transition metals.

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

**341. Transition Metal Activation and Functionalization of Carbon-Hydrogen Bonds**  
W.D. Jones, Dept. of Chemistry **\$65,900**

This research is directed toward the activation and cleavage of carbon-hydrogen bonds by homogeneous transition metal compounds. The possibilities for forming hydridometal-aryl and -alkyl complexes and trapping these intermediates with isocyanides, olefins or acetylenes is under investigation. A reaction sequence involving trapping, insertion, and reductive elimina-

tion would yield imine or styrene products. These systems have the added feature that they can be catalytic, as the metal complexes are not consumed and the overall thermodynamics are favorable. The complexes  $\text{CpRe}(\text{PPh}_3)_2\text{H}_2$  and  $\text{Fe}(\text{PMe}_3)_2(\text{CNR})_3$  both show behavior with arenes that is consistent with the functionalization scheme. The former complex catalyzes the insertion of ethylene into the C-H bond of benzene, producing ethylbenzene; the latter complex stoichiometrically converts benzene to aldimine. Other studies in progress involve the mechanism and thermodynamics of intra- and intermolecular alkane and arene C-H bond activation in the series of complexes  $(\text{C}_5\text{Me}_5)\text{Rh}(\text{PMe}_2\text{R})(\text{R}')(\text{H})$ . For  $\text{R}=\text{Me}$  there is little kinetic selectivity for the activation of arenes versus alkanes, although there is a large thermodynamic selectivity favoring arene activation. Current work with  $\text{R}=\text{benzyl}$  indicates that there is little kinetic selectivity for intramolecular cyclometallation versus intermolecular activation of neat benzene solvent, but that the cyclometallated species is favored thermodynamically.

**University of Texas**  
Austin, Texas 78712

**342. Study of Synthesis Gas Conversion Over Metal Oxides**  
*J.G. Ekerdt, Dept. of Chemical Engineering* **\$53,400**

The goals of this program 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. Direct CO hydrogenation into branched alkanes, isosynthesis, is being investigated over zirconium dioxide. High pressure (35 atm) rate studies are performed to examine the primary products and establish the kinetics of  $\text{C}_1$  to  $\text{C}_4$  isosynthesis product formation. Atmospheric studies are performed to determine the catalytic reactions between CO,  $\text{CO}_2$ ,  $\text{H}_2$ , and the zirconium dioxide surface and to gain insight into the reactions which initiate isosynthesis. The results from both pressure regimes will be used to propose a mechanism for isosynthesis. The mechanism will be used as the basis for designing experiments directed toward the causes for metal oxide activity and selectivity.

**University of Utah**  
Salt Lake City, Utah 84112

**343. Ligand Intermediates in Metal Catalyzed CO Reduction**  
*J.A. Gladysz, Dept. of Chemistry* **\$91,800**

This research program has as its basic goal the synthesis and study of homogeneous complexes containing ligand types (e.g.,  $-\text{CHO}$ ,  $=\text{CHOH}$ ,  $=\text{CH}_2\text{OH}$ ,  $\text{C}$ ,  $\text{CH}$ ,  $=\text{CH}_2$ ,  $\text{H}_2\text{C}=\text{O}$ ,  $-\text{OCHO}$ , and so forth) believed to be intermediate in the metal catalyzed conversion of  $\text{CO}/\text{H}_2$  gas mixtures to organic molecules. Mechanistic understanding of the steps involved in catalytic CO reduction, and insight needed for the design of new catalysts, is sought. Current studies are making extensive use of optically active substrates derived from easily resolved  $[(\text{H}-\text{C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CO})]^+\text{BF}_4^-$ . For instance, methyldene

$(+)-(\text{S})-[(\text{H}-\text{C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(=\text{CH}_2)]^+\text{PF}_6^-$  ( $(+)-(\text{S})-1$ ) couples to ethylene complex  $(+)-(\text{R})-[(\text{H}-\text{C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{CH}_2)]^+\text{PF}_6^-$  with retention. This coupling also exhibits a remarkable degree of enantiomer self-recognition: the  $(+)-(\text{S})-1$  couples virtually exclusively with  $(+)-(\text{S})-1$ , and  $(-)-(\text{R})-1$  couples virtually exclusively with  $(-)-(\text{R})-1$ . The formate  $(+)-(\text{R})-(\text{H}-\text{C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{OCHO})$  decarboxylates at  $70-130^\circ\text{C}$  to hydride  $(+)-(\text{S})-(\text{H}-\text{C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H})$  with retention. An isolable manganese  $\alpha$ -hydroxyalkyl complex has recently been observed to undergo carbonylation to a  $\alpha$ -hydroxyacyl complex.

**344. Liquid and Solid Carbon-13 Magnetic Resonance Study of Hydrocarbons and Related Substances**  
*D.M. Grant, R.J. Pugmire, Dept. of Chemistry* **\$95,000**

Work continues to focus on both liquid and solid state NMR methods applied to the characterization of carbonaceous compounds and materials important in the energy industry. Model organic compounds provide substance upon which the methods may be calibrated and standardized. Hydroaromatics, coal macerals, various fossil fuels and their precursors provide the main focus of this work. Exploratory research on single crystals has been initiated in an attempt to better understand the important dipolar dephasing experiment which is being used extensively on powders such as coals, and so forth. The dipolar dephasing rate depends on the orientation of the carbon-hydrogen bonds and basic single crystal work on hydrocarbons will provide definitive information required to get good intensity data on solid state powders. The development of an ultrahigh speed rotor is well under way. By decreasing the outer diameter, it has been possible to increase the rotation rates to 8 KHz. Reduced rotor diameters will also allow for increasing radio frequency fields at reduced power dissipation. Both effects should enhance our ability to obtain chemical-shift/J-coupled two dimensional spectra in solids.

**345. Comprehensive Characterization Studies of Sulfided Molybdena Catalysts**  
*F.E. Massoth, Dept. of Fuels Engineering* **\$75,500**

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 (viz., structure, dispersion, active sites) of the active phase. Several newer techniques not available or not employed 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,  $\text{H}_2\text{S}^{35}$  exchange, ESCA, XRD, and 'SH' content. The catalytic activities of the catalysts will be measured for HDS, HDN, hydrogenation, and hydrocracking employing model compounds representative of these catalytic functions. This program should provide insight into the major factors responsible for catalytic activity of the various functions present in these complex catalysts.

**University of Wisconsin  
Madison, Wisconsin 53706**

**346. Mechanistic Studies Related to the Metal Catalyzed Hydrogenation of Carbon Monoxide to Hydrocarbons**  
*C.P. Casey, Dept. of Chemistry* **\$103,000**

The synthesis of organometallic compounds which contain functional groups similar to those proposed in homogeneous and heterogeneous catalyzed carbon monoxide reduction is being carried out, so that the properties and reactions of these species can be studied. This basic information should contribute to the understanding and eventual design of catalysts for the reduction of carbon monoxide. Detailed studies of the synthesis and reactions of metal formyl compounds (M-CO-H) and hydroxymethyl metal compounds (MCH<sub>2</sub>OH) [models for intermediates in the homogeneous hydrogenation of CO] are being carried out. Compounds with CH<sub>3</sub>, CH<sub>2</sub>, and CH groups bridging between two iron atoms have been synthesized as models for intermediates in the heterogeneous catalysis of CO hydrogenation. Carbon-carbon bond forming reactions of the CH compounds with alkenes and with CO are being explored. Several heterobimetallic compounds linked by a heterodifunctional ligand have been synthesized. Their reaction with hydrogen is being studied as a possible route to heterobimetallic dihydrides that might serve as catalysts for CO reduction. New compounds with directly bonded early and late transition metals have been synthesized and their fundamental chemistry is being explored; for example, (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Zr[Ru(CO)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>]<sub>2</sub> has been made and its reactions with CO and H<sub>2</sub> are under investigation.

**347. Acid Sites Formed By Doping Cations Onto Oxide Surfaces: Theoretical Aspects and Experimental Studies**  
*J.A. Dumesic, Dept. of Chemical Engineering* **\$61,200**

Our current research involves the characterization of acid sites formed by doping transition metal cations onto oxide surfaces. Our initial studies in this direction are focused on the use of iron as the dopant and irreducible oxides as supports (e.g., silica, magnesia, alumina). Adsorption of basic molecules is being used to probe the number of acid sites formed in this manner. Combined with infrared spectroscopy and temperature programmed desorption, this also provides information about the nature and the strength of the acid sites. One objective of our present studies is to relate the chemical properties of the acid sites to solid state structure. In this respect, Moessbauer spectroscopy is being used to determine the oxidation state and coordination number of the iron cations on the different oxide support surfaces after various catalyst pretreatments. We are assessing the catalytic consequences of our research using the decomposition of isopropanol as a catalytic probe reaction.

**Wayne State University  
Detroit, Michigan 48202**

**348. Synthesis, Static, and Reactive Characterization of Supported Organometallics**  
*A. Brenner, Dept. of Chemistry* **\$83,000**

The nature and activity of catalysts derived from supported carbonyl complexes is being studied. The technique of temperature programmed decomposition has been applied to examine the

nature of the bonding of Mo(CO)<sub>6</sub> to a variety of zeolites as a function of structure (A, X, Y, ZSM-5), Si/Al ratio, and cation identity (H<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>) of a zeolite. The use of photolysis as an alternative to thermal activation is also being studied. Both Fe(CO)<sub>5</sub> and Mo(CO)<sub>6</sub> can be almost completely decarbonylated when supported on silica to produce a highly dispersed metallic catalyst. Exhaustive decarbonylation is not yet possible when supported on alumina. Catalysts produced by photolysis have been tested for the ability to equilibrate a H<sub>2</sub>-D<sub>2</sub> mixture. The catalysts have very high activity for this reaction. Since the reaction is usually much faster on metal surfaces than on oxides or molecular complexes, it is a useful probe of the nature of the active sites on a catalyst. Structure-activity studies for benzene hydrogenation are also being developed. The analysis system for Fischer-Tropsch synthesis has been improved and it is now found that over W(CO)<sub>6</sub>Al<sub>2</sub>O<sub>3</sub> the rate of reaction is fifty-fold higher than that over a traditional catalyst (derived from WO<sub>3</sub>) and the products are primarily methane, ethane, and propane.

**Yale University  
New Haven, Connecticut 06511**

**349. Studies of the Hydrogenation of Small Unsaturated Molecules Using Organometallic Cluster Compounds As Catalysts**  
*R.D. Adams, Dept. of Chemistry* **\$23,800**  
(3 mo.)

This research project is focused on the mechanisms of activation and hydrogenation of small heteronuclear unsaturated molecules like CO and CO<sub>2</sub> by polynuclear transition metal complexes. Special emphasis is being placed on the importance of multinuclear bridging coordination forms in ligand activation. The products of selected reaction sequences are being investigated by IR and NMR spectroscopies, and are being structurally characterized by single-crystal x-ray diffraction analyses.

**350. Studies in Carbon Carbon Bond Activation**  
*R.H. Crabtree, Dept. of Chemistry* **\$70,000**  
(8 mo.)

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 have shown that cyclopentanes can be dehydrogenated to cyclopentadienyl complexes by IrH<sub>2</sub>(solvent)<sub>2</sub>L<sub>2</sub> cations. One proposal is to attempt the reaction with *gem*-dimethylcyclopentanes to see if a dimethylcyclopentadienyl complex can be obtained. This should subsequently undergo alkyl transfer to give a methyl iridium cyclopentadienyl complex. Other related strategies are discussed as well as possible extensions to catalytic systems ("homogeneous reforming").

**351. Selectivity, Activity, and Metal-Support Interactions of Rh Bimetallic Catalysts**  
*G.L. Haller, Dept. of Chemical Engineering* **\$80,000**

This research program is designed to investigate the effects of a modifying second metal and/or the support on the selectivity and activity of Rh supported catalysts. The systems of current interest are Rh/TiO<sub>2</sub>, Rh/V<sub>2</sub>O<sub>3</sub>, and Rh-Pt bimetallics supported on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>. Rh-Pt is unique among the

noble intergroup VIII bimetallic catalysts by virtue of the extremes of the activity of the individual components (for alkane hydrogenolysis and isomerization) and the potential for the formation of homogeneous bimetallic particles. The structure of the Rh bimetallic catalysts on various supports will be determined using XPS, EXAFS, NMR, and complementary chemisorption and catalytic test reactions. Among the catalytic test reactions will be hydrogenolysis, alkane isomerization, and CO/H<sub>2</sub> reactions.

- 352. *The Role of d-Electrons in Chemisorption and Metal Support Interactions Studied By Electron Spectroscopy***  
*V.E. Henrich, Dept. of Applied Physics* **\$60,000**

This research program utilizes model supported catalysts (small Rh particles desposited *in situ* on well characterized TiO<sub>2</sub> single-crystal surfaces) and surface-sensitive electron spectroscopies, including photoemission and Auger spectroscopy, to examine the role of d-electrons and support electronic structure in strong metal/support interactions. Core level binding energies of the Rh atoms measured by photoemission are found to depend upon particle size. The primary cause is believed to be changes in screening of the core hole, although changes in the valence state of the Rh atoms cannot be ruled out. Heating the model catalyst to 400°C results in a decrease in the amount of exposed Rh and supression of CO chemisorption. Inert gas sputter profiling of the catalysts before and after such reduction indicates that the Rh particles become partially covered by an oxide of Ti. Removal of the Ti oxides by inert gas sputtering restores CO chemisorption. The effects of various catalyst treatments are currently being investigated in order to correlate the electronic and geometric effects that have been observed to strong metal/support interactions.

- 353. *Energies of Organic Compounds***  
*K.B. Wiberg, Dept. of Chemistry* **\$88,000**

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 semi-empirical 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 (RHF) are being 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 which are used in molecular mechanics.

## Separation and Analysis

**Aerospace Corporation**  
EL Segundo, California 90245

- 354. *Laser Fluorescence Studies of Metallic Ions in Flames For Improved Detection***  
*F.E. Hovis, J.A. Gelbwachs,* **\$27,800**  
*Chemistry & Physics Lab.*

The use of fluorescence methods on neutral metal atoms in flames is a well established analytical technique. We propose to investigate laser induced fluorescence of metallic ions in high temperature flames for analytical applications. The first study involves the direct laser excitation of ionic fluorescence of the alkaline earth metals. A second experiment investigates neutral-ion energy transfer in metals as a means of sensitized ion fluorescence for multielement analysis. The use of sensitized ion fluorescence would allow simultaneous analysis of several metals using a single laser excitation line. The use of neutral-ion energy transfer is anticipated to yield superior detection limits to neutral-neutral energy transfer, and to have good potential as a practical analytical tool. These studies will yield information of both practical and fundamental interest.

- 355. *Isotopically Selective, Two-Step, Laser Photodissociation of Molecules***  
*P.F. Zittel, Chemistry and Physics Lab.* **\$115,000**

This research project is directed toward understanding those 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. A computer-interfaced, dual beam, IR absorption apparatus is used to measure the absorption of intense IR laser pulses by the target molecule as a function of pressure and laser fluence. Mass spectrometric analysis of the photoproducts of the subsequent UV photodissociation step reveals the effect of vibrational excitation on the photodissociation cross section, and gives 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 O, C, and S, and to a determination of the 249 nm photodissociation cross section of the  $\nu_1$  and  $2\nu_2$  vibrational states of OCS. Rate constants for various vibrational energy transfer processes and chemical reactions are also inferred from isotope enrichment measures.

**Bend Research, Inc.**  
Bend, Oregon 97701

- 356. *Fundamentals of Coupled-Transport Membranes***  
*D. Friesen, Division of Membrane Separation* **\$89,900**

The project objective is to study the fundamentals of coupled-transport membranes as applied to the concentration and separation of uranium and other metals. Coupled-transport membranes consist of a water-immiscible, liquid complexing agent held by capillary forces in the pores of a microporous polymeric support. This membrane separates two aqueous solutions of unequal concentrations. The complexing agent can pick up ions on one side of the membrane and carry them across the membrane by diffusion in the form of a neutral complex. Metal ions

can be transported from a dilute to a concentrated solution by coupling their flow to that of another ionic species. The membranes are also selective due to the selectivity of the complexing agent toward one metal ion over other similar metal ions. Thus, coupled transport is of potentially practical value in hydrometallurgy, and in the treatment of radioactive wastes. Current efforts are focused on studying and improving the long-term performance of coupled-transport membranes. A model has been developed that is consistent with observed membrane performance. Based on this model, substantial progress has been made in developing membranes with commercially practical lifetimes.

### Brigham Young University Provo, Utah 84602

357. *Separation of Selected Cations By Liquid Membranes*  
J.J. Christensen, Dept. of Chemical Engineering \$68,900

Macrocyclic-mediated cation transport using bulk, emulsion, and lipid vesicle liquid membrane systems is being investigated and modeled. In water-halocarbon-water bulk liquid membranes, transport is being studied of alkali and alkaline earth metal ions as a function of the halocarbon component and of Ag<sup>+</sup>-K<sup>+</sup> mixtures where the relative Ag<sup>+</sup> and K<sup>+</sup> concentrations have been varied over a wide concentration range. The relative fluxes of cations from cation mixtures in water-toluene-water emulsion membrane systems is under investigation using the carrier dicyclohexano-18-crown-6, and various complexing anions in the interior receiving phase. The transport in these emulsion systems of amphoteric metals as anionic species coupled to a pH gradient across the membrane is also being studied. Dicyclohexano-18-crown-6 and other macrocycles have been incorporated into phospholipid vesicles as a means of making the vesicles selectively permeable to cations. The chemical and thermodynamic characteristics of the interaction, individually and as mixtures, of Pb<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup> with these vesicles is being investigated.

### Brown University Providence, Rhode Island 02912

358. *Photochemical Generation of the Optoacoustic Effect*  
G.J. Diebold, Dept. of Chemistry \$72,200

Photochemical generation of the optoacoustic effect is being investigated. Chain reactions can be studied by recording the amplitude and phase of the optoacoustic signal. As small amounts of different chemical species are added to systems undergoing photochemical chain reactions, the optoacoustic signal is either enhanced or diminished according to the effect of the added species on the chain length and overall reaction exothermicity. Inhibitors act to shorten chain lengths which is observed experimentally as a dramatic reduction in the chemically amplified signal recorded in a lockin amplifier. It is possible to test different models of the mechanism of inhibitions by comparison of the experimental optoacoustic signal amplitude with the predictions of a kinetic model. The objective of this research is to investigate the optoacoustic effect with its inherent high sensitivity and unique response to energy release as a technique for chemical analysis.

### Calspan Advanced Technology Center Buffalo, New York 14225

359. *Energy Transfer and Reaction Kinetics of Vibrationally Pumped Molecules*  
J.W. Rich, Dept. of Physical Sciences \$57,000

This is a project for experimental and analytical research into energy transfer and reaction kinetics of vibration-to-vibration (V-V) pumped molecules. Extreme V-V pumped vibrational population distributions in CO, NO, and other gaseous species are produced by optical excitation. Special emphasis is being placed on isotopic enrichment reactions of V-V pumped CO, which yield products enriched in <sup>13</sup>C, <sup>17</sup>O, and <sup>18</sup>O. Processes limiting vibrational up-pumping in CO and NO are being studied, especially vibration-to-electronic energy transfer from the pumped ground electronic state of these molecules to low lying excited electronic states. The rate equation kinetic modeling of these processes is being developed.

### Columbia University New York, New York 10027

360. *Utilization of Magnetic Effects As a Means of Isotope Enrichment*  
N.J. Turro, Dept. of Chemistry \$69,900

This research project is directed toward the development of 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 which possess a finite magnetic moment from those which do not possess a magnetic moment. Successful systems have been designed for separation of <sup>13</sup>C (a magnetic isotope) from <sup>12</sup>C (a non-magnetic isotope), and for the separation of <sup>17</sup>O (a magnetic isotope) from <sup>16</sup>O and <sup>18</sup>O (non-magnetic isotopes). The restricted space provided by porous silica has proven to be an excellent environment for efficient separation of <sup>13</sup>C and <sup>12</sup>C based on the photolysis of dibenzyl ketone. The efficiency of enrichment as a function of pore size is being investigated. It should now be possible to design a practical system to separate these isotopes.

### George Washington University Washington, District of Columbia 20052

361. *New High Temperature Plasmas and Sample Introduction Systems For Analytical Atomic Emission Spectrometry*  
A. Montaser, Dept. of Chemistry \$58,100

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 either now or are likely to arise in the future in the various fields of energy generation, environmental pollution, biomedicine, and nutrition. Emphasis is being placed on: (1) generation and fundamental investigation of annular plasmas that are suitable for the excitation of high energy spectral lines, with the intent of enhancing the detecting powers for a number of elements; (2) generation of plasmas that require low gas flows and low input power, with the intent of decreasing the cost of analyt-

ical determination; and (3) development and characterization of new sample introduction systems that consume microliter or microgram quantities of samples. Investigations include the fundamental principles behind the measurements, the evaluation of the analytical potentials of the devices developed, and the demonstration of the analytical methods in representative samples.

### **Kent State University** **Kent, Ohio 44242**

#### **362. Adsorption and Desorption of Hydrocarbons At Low Concentrations** *R. Madey, Dept. of Physics* **\$71,000**

The aim of this research is to study the adsorption and diffusion of hydrocarbon 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. An objective of this study is to provide a quantitative explanation of interference phenomena. The approach will be to obtain binary adsorption isotherms, to examine the mechanisms of intraparticle diffusion and longitudinal diffusion of the system, and to study the mathematical characteristics of the differential equation that governs the system.

### **National Bureau of Standards** **Washington, District of Columbia 20234**

#### **363. Competitive Ion Kinetics in Direct Mass Spectrometric Organic Speciation** *L.W. Sieck, Center for Chemical Physics* **\$131,000**

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 which 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 NBS pulsed high pressure mass spectrometer system as the prime facility, and an ion cyclotron resonance instrument is also available. Work-in-progress includes determinations of enthalpies of protonation, hydration, and solvation of complex amines, ethers, and sulfur compounds, as well as systematic studies of the unimolecular kinetics associated with ion pyrolysis. Analogous measurements involving complex negative ions, particularly their thermal stability and reaction kinetics, are also currently receiving emphasis.

### **Purdue University** **West Lafayette, Indiana 47907**

#### **364. Reactions of Gaseous Metal Ions/Their Clusters in the Gas Phase Using Laser Ionization: Ion Cyclotron Resonance Spectroscopy** *B.S. Freiser, Dept. of Chemistry* **\$85,000**

A laser ionization source is used in conjunction with ion cyclotron resonance spectroscopy to generate and study the gas phase chemistry of simple metal ions and their clusters. Using this technique, metal ions are generated directly by focusing a high-powered pulsed laser onto the pure metal. The goals of this work have been threefold: (1) determination of fundamental reaction mechanisms and trends in reactivity; (2) comparison of gas phase to solution phase results; and (3) development of metal ions as selective chemical ionization reagents. These goals have been pursued thus far in extensive studies of  $\text{Cu}^+$  with esters and ketones, on  $\text{Fe}^+$  with ethers and ketones, and on  $\text{Fe}^+$ ,  $\text{Ti}^+$ ,  $\text{Co}^+$ ,  $\text{Ni}^+$ ,  $\text{Rh}^+$ ,  $\text{V}^+$ ,  $\text{Y}^+$ , and  $\text{Sc}^+$  with hydrocarbons. In addition, work has been started on the effect of ligands on metal ion reactivity. Studies of  $\text{M-X}^+$  ions, where  $\text{X}=\text{O}$ ,  $\text{S}$ ,  $\text{CH}_2$ ,  $\text{CH}_3$ , and  $\text{C}_2\text{H}_4$ , for example, are well under way. This work has been catalyzed further with the acquisition of a Nicolet Fourier transform mass spectrometer (FTMS). Of particular importance is the application of collision-induced dissociation, using FTMS to elucidate ion structures and reaction mechanisms.

### **San Diego State University** **San Diego, California 92182**

#### **365. Development and Optimization of Methodologies For Analysis of Complex Hydrocarbon Mixtures** *R.J. Laub, Dept. of Chemistry* **\$65,000**

The goals of this project comprise exploration and further clarification of optimization methodologies for gas- and liquid-chromatographic separations of complex hydrocarbon mixtures. Emphasis is being placed at present on the kinetics of mass transfer, temperature effects, and mobile-phase composition in microbore-, conventional-bore, and rotating-disk thin-layer liquid-chromatographic techniques with silica, reversed-phase silica, and alumina adsorbents. Also being studied are metal-modified silica LC packings, including *in situ* generation, and alteration of the adsorbent surface. The utility of binary carriers in gas chromatography is being examined, where the second-interaction virial coefficients are predicted in advance from the McGlashan-Potter equation. Solute retentions are then calculated, where the separations achieved are a function both of the carrier pressure and composition. Work on establishment of a standard set of stationary phases for gas chromatography is being continued, where emphasis is being placed on newly-synthesized mesomorphic polysiloxane (MEPSIL) solvents.

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

#### **366. Fundamental Studies in Isotope Chemistry** *J. Bigeleisen, Dept. of Chemistry* **\$64,000**

Experimental and theoretical investigations are made of isotope effects in chemical and physical processes. When appropriate, applications are made to isotope separation processes and nuclear fuel cycles. Calculations have been made of the

expected chemical properties of super-heavy isotopes of hydrogen, carbon, selenium, and uranium as a guide in the search for such particles. Detailed calculations have been made of the separation expected of superheavy isotopic forms of CO by fractional distillation. Relations between the isotope chemistry of oxygen and molecular structure are being studied. Regularities are found by an analysis of the effect of isotopic substitution on the entropies and enthalpies of formation of the compound from the gaseous oxygen atom.

### 367. *Stable Isotope Studies*

*T. Ishida, Dept. of Chemistry* **\$81,600**

This project consists of basic studies of isotopic effects (IE) and applications to problems of stable isotope fractionation. With an aim at elucidating the nature of weak hydrogen bond-like interactions involving fluorine atoms in the liquids, the anomalously large H/D-vapor pressure isotope effect (VPIE) and small  $^{12}\text{C}/^{13}\text{C}$ -VPIE in liquid methylene fluoride are correlated with intermolecular forces in the liquid, and they are compared with the VPIEs of other liquid fluoromethanes in the light of the extended cell model vibrational analyses and *ab initio* molecular orbital calculations. The  $^{14}\text{N}/^{15}\text{N}$ - and H/D-VPIEs measured for liquid and solid ammonia are analyzed to learn more critically about the nature of liquid ammonia, the material of importance in the heavy water production technology. Attempts are made to develop an ammonia-phobic heterogeneous catalyst for the H/D exchange between ammonia and hydrogen. The marked discrepancy between theoretical predictions and experiments on the pressure-dependence of the effective separation factor in the  $^{15}\text{N}$ -enrichment system of nitric oxide/dinitrogen trioxide is investigated in the light of recent spectroscopic data. Based on the zero-point (ZPE) expansion obtained last year, additivity rules and contribution tables are developed for the IE in ZPE of various homologs.

## Syracuse University

Syracuse, New York 13201

### 368. *Mechanisms of Gas Permeation Through Polymer Membranes*

*S.A. Stern, Dept. of Chemical Engineering & Material Sciences* **\$75,000**

The objective of this study is to obtain a basic understanding of the mechanisms of gas permeation through nonporous polymer membranes. A free-volume model of gas permeation was found to describe satisfactorily the transport of many gases, and of a number of gas mixtures through polyethylene membranes. The model is applicable at temperatures above  $T_g$ , the glass transition of the polymer, over a wide range of pressures. The validity of the model is being tested with other polymer membranes. Simple correlations of free-volume parameters have been developed. These correlations permit the prediction of diffusion and permeability coefficients for many gases and components of gas mixtures. Solubility data are also required for this purpose. The gas permeation model has been extended to glassy polymers by incorporating in it the dual-sorption behavior observed below  $T_g$ . The extended model is being examined by means of time-lag and absorption-desorption measurements, with a number of gases in poly(*n*-butyl methacrylate) over a temperature range encompassing  $T_g$ .

### 369. *Selective Metal Ion Extraction For Multiple Ion Liquid-Liquid Exchange Reactions*

*L.L. Tavlarides, Dept. of Chemical Engineering & Material Sciences* **\$77,000**

This research in hydrometallurgical solvent extraction is to develop a fundamental means to predict selectivity during simultaneous solvent extraction of multiple metal ions when kinetic rates and thermodynamic equilibria do not favor the desired metal. The chemical kinetics and thermodynamic chemical equilibria models for the system copper-iron acid sulfate solutions extracted by  $\beta$ -alkenyl-8-hydroxy quinoline-xylene system are being determined. A kinetic model for the initial forward rate of the iron extraction reaction is proposed. The model considers adsorption of HR, HR protonation, and that the formation of  $\text{FeR}_2$  is the RDS. Kinetic data for the stripping reaction have been obtained and are being evaluated. Extraction experiments were conducted on a specially equipped 1-liter flow system with facilities for drop size measurements and *in situ* sampling of both phases for the iron system. A Monte Carlo simulation algorithm is employed to model droplet dynamics and predict extractor performance for the iron sulfate system as a function of system physico-chemical properties and operating parameters such as residence time, power input, dispersed phase fraction, and feed composition. The modeling includes aqueous phase equilibria and the reaction kinetics determined previously. Results suggest the validity of such models to predict extraction efficiencies of complex hydrometallurgical solvent extraction systems.

### 370. *Particle Deposition in Granular Media*

*C. Tien, Dept. of Chemical Engineering & Material Sciences* **\$104,000**

This research is intended to obtain fundamental understanding of various phenomena arising from the flow of aerosol suspensions through, and the deposition of aerosols in, granular media. The study is focused on the following areas: (1) experimental study of the transient state behavior of aerosol filtration in experimental filters; (2) the study of aerosol collection in magnetically stabilized fluidized filters and its modeling; and (3) the application of a specially designed two dimensional filter for *in situ* observation of the change of media structure due to the retention of aerosol particles.

## Texas A & M University

College Station, Texas 77843-3255

### 371. *Investigations On Multiphoton Ionization and Fast-beam Photodissociation Spectroscopy*

*D.H. Russell, Dept. of Chemistry* **\$90,000**

The emphasis of this research program is the development of combined laser-mass spectrometry methods for probing the dynamics of dissociation reactions. The experimental hardware and techniques are being developed using model chemical systems which have been characterized by other experimental methods (e.g.,  $\text{C}_6\text{H}_6^+\oplus$ ,  $\text{C}_4\text{H}_6^+\oplus$ ,  $\text{C}_4\text{H}_4^+\oplus$ , and so forth). Following these preliminary investigations, the experimental capabilities will be applied to chemical systems in which this approach provides unique or unusual capabilities. These latter studies emphasize the structural characterization of large molecular systems (1,000-10,000 a.m.u.). These large molecules are ionized using fast-neutrals (8-10 KeV Xe) and fast-ions

(8-10 KeV Cs<sup>+</sup>)-fast-atom bombardment (FAB) and secondary ion mass spectrometry (SIMS)-directly from the solid state. Also, these latter studies will be performed using a high resolution tandem mass spectrometer (Kratos MS-50TA), with high mass range capabilities (3,000-5,000 a.m.u.) and a Fourier transform mass spectrometer (Nicolet FTMS-2,000).

**Texas Tech University**  
**Lubbock, Texas 79409**

- 372. Use of Functionalized Surfactants in Flame Atomic and Luminescence Analysis**  
*D.W. Armstrong, Dept. of Chemistry* **\$87,000**

Nine functionalized surfactants are to be used in this project to enhance the sensitivity and improve the selectivity of flame atomic spectrometry (FAS) and luminescence methods of analysis. Conventional bulk industrial surfactants such as sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) have been used with some success in improving both methods (particularly luminescence). The mechanism by which these surfactants produce their effects has been the subject of some controversy. By using our first generation of specially designed surfactants, we hope to improve the sensitivity of the aforementioned techniques an order of magnitude over that now possible. Through these surfactants, one should be able to achieve a degree of selectivity (for these methods) approaching that of chromatography. Lastly, this study should remove any doubt as to the mechanism by which surfactants produce signal enhancements in FAS and provide additional information on the feasibility and mechanism of micelle mediated luminescence.

- 373. Metal Ion Complexation By Ionic Crown Ethers**  
*R.A. Bartsch, Dept. of Chemistry* **\$112,500**

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 selectivities of these lipophilic ionizable crown ethers in competitive solvent extraction, liquid surfactant (emulsion) extraction, and bulk liquid membrane transport of alkali metal, alkaline earth, and transition metal cations are being assessed.

- 374. Novel Approaches to Ionic Chromatography**  
*P.K. Dasgupta, Dept. of Chemistry* **\$85,000**

The objective of this research is to develop analytical methodology for high resolution, high sensitivity chromatographic analysis of ions. The approaches being pursued include: (1) use of filament filled helical ion exchanger membranes and double annular membrane geometries for continuous ion exchange; (2) utilization of the Debye-Falkenhagen effect in high speed frequency swept conductance detection and unambiguous detection of the nature of the ion from a derivative plot; (3) use of multidimen-

sional spectral array detectors in conjunction with reverse phase packings and chromogenic ligands as eluents for transition metal analysis; and (4) exploration of annular helical capillary columns for very high resolution chromatographic work. Currently, the major effort involves use of highly lipophilic ions as ion interaction reagents (IIR) injected into the chromatographic system as programmed pulses. The IIR are eventually completely exchanged by a helical membrane based exchanger.

**University of Arizona**  
**Tucson, Arizona 85721**

- 375. Chelating Extractants of Improved Selectivity**  
*H. Freiser, Dept. of Chemistry* **\$82,400**

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 represents one approach to the elucidation of molecular parameters. Study of the extraction equilibria for representative trivalent lanthanides with selected members of chelating extractants of the N-acylphenylhydroxylamine, 8-quinolinol, acylpyrazolone, and other families is being used, both because they include some likely candidate extractants and because present gaps in fundamental data required to apply pattern recognition are thereby being eliminated.

**University of California/Irvine**  
**Irvine, California 92717**

- 376. Studies of Isotopic Mass Effects in Chemistry**  
*M. Wolfsberg, Dept. of Chemistry* **\$80,000**

This project deals with theoretical studies of isotopic mass effects on molecular properties. Such work is usually carried out within the framework of the Born-Oppenheimer approximation. Exact expressions for the complete quantum mechanical Hamiltonian operator of molecules are being constructed to study this approximation. Statistical mechanical calculations of isotope effects on a variety of molecular properties require a knowledge of rotational-vibrational energies of molecules and of isotope effects on these energies. Such energies are being calculated by the variational method for formaldehyde, water, and other molecules. The tunneling phenomenon and isotope effects on tunneling are being studied by an investigation of the vibrational energy levels of molecules with double-minimum potentials, in particular ammonia. Molecular dynamics calculations are being carried out on aqueous solutions of rare gases and of diatomic molecules such as nitrogen, to elucidate isotope effects on Henry's law constants as well as to study the structure of these solutions. The difference between gas phase and condensed phase infrared spectra is being studied in connection with isotope effects on vapor pressures.

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

- 377. Multiheteromacrocycles That Complex Metal Ions**

*D.J. Cram, Dept. of Chemistry* **\$125,000**

This research involves the design, synthesis, and evaluation of cyclic and multicyclic organic compounds that selectively complex metal salts and solubilize them in organic solvents. Spherands are synthetic ligand systems that in the uncomplexed state contain enforced cavities lined with electron pairs. Rigid cyclic frameworks support attached heteroelements so that their unshared electron pairs occupy convergently arranged orbitals. Spherands are being studied whose cycles are composed of six to eight six-membered rings bonded to one another at their 1,3-positions, and which carry substituents in their 2-positions. Chorospherands are part crown and part spherand, and cryptospherands are part cryptand and part spherand. Spherands, chorospherands, and cryptospherands are being studied which contain anisyl, pyridine, pyridine oxide, benzoquinone, thioanisyl, cyclic urea, phenol, and benzenecarboxylic ester units. Complexes are designed with the help of CPK molecular models. Synthetic methods are then developed by which the ligand systems are prepared. The compounds are then tested for their metal ion-binding abilities and specificities.

**University of Georgia**  
Athens, Georgia 30605

**378. Study of Mechanisms of Hydrogen Diffusion in Separation Devices**  
*M.H. Lee, Dept. of Physics and Astronomy* **\$77,000**

This study centers on separating hydrogen from mixtures of light gases by means of diffusion through metals. The hydrogen diffusion is highly selective, showing nonclassical behavior. The metal-hydrogen systems have mean-field critical dynamics. To describe the hydrogen diffusion, a quantum mechanical model is constructed, based on cluster formation. The diffusion is regarded as a collective movement of clusters. The sizes of these clusters depend on interatomic forces and particle statistics. The observed reversed isotope effect is explained by different degrees of cluster formation in hydrogen and deuterium. The diffusion constants are calculated by solving the generalized Langevin equation via the methods of recurrence relations recently developed by us.

**379. Fundamental Studies of Separation Processes**  
*L.B. Rogers, Dept. of Chemistry* **\$78,000**

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. Non-porphyrin 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. A second area involves the identification of those non-porphyrin compounds using a variety of techniques. The third area is concerned with recycle chromatography, a promising approach to separations of isotopic species.

**University of Houston**  
Houston, Texas 77004

**380. Mechanisms of Cake Filtration**  
*F.M. Tiller, M. Tadros, Dept. of Chemical Engineering* **\$160,000**

This project is aimed at developing the theory of particulate separation involving compressible, porous beds or sediments as found in filtration, centrifugation, and sedimentation. A key feature of the investigation involves close collaboration between the University of Houston and Martin-Marietta Laboratories. Generation of reliable data and integration of the areas of pre-treatment, thickening, and separation are objectives of the research. A rough predictive method for calculating parameters involved 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 developed. Initial cake structure of deposits as affected by surface charge, suspension concentration, and agitation are being studied in relation to resistance to flow. Pressure distributions are used to study flow mechanisms and fine particle migration. The theory of centrifugal filtration of compressible cakes has been developed.

**University of Illinois**  
Urbana, Illinois 61801

**381. Theta Pinch Discharges For Solids Vaporization and Elemental Chemical Analysis**  
*A. Scheeline, School of Chemical Sciences* **\$66,000**

A pulsed, magnetically constricted plasma (theta pinch) is being used for elemental chemical analysis. A 0.5-1.0 kJ discharge with rise time 2 microseconds is employed to heat and compress a plasma of either argon or helium. Various sample forms are being tested, as there is interaction between the shape of the sample, plasma formation, and plasma/sample interaction. Spatially resolved spectra are being exploited to assist in resolving continuum and line background from analyte emission. Time resolution will also be performed. Our goal is to design a discharge system which can vaporize high melting solids, whether conducting or non-conducting, for matrix free determinations of elemental composition of the solids being studied. Because the plasma survives for only a few microseconds, only the surface of the sample is likely to be attacked by the discharge. Possibilities of controlling the depth of sampling and the area over which sampling occurs will be explored.

**University of Minnesota**  
Minneapolis, Minnesota 55455

**382. Continuous Reaction Chromatography**  
*R. Aris, R.W. Carr, Dept. of Chem. Engineering and Materials Science* **\$70,000**

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 reac-

tion-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 done. 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 currently being investigated both theoretically and experimentally.

**383. Interfacial Chemistry in Solvent Extraction Systems**

*R.D. Neuman, Dept. of Forest Products* **\$85,000**

Laser light-scattering techniques, in addition to classical surface chemical methods, are being employed to investigate the interfacial behavior of extractant molecules and to further our understanding of the role of interfacial chemistry in solvent extraction systems. This program is a coordinated effort to correlate the interfacial properties of extractant films with mass transfer and coalescence rates. Studies examining the effect of pH and extractant (HDEHP) concentration on interfacial tension measurements are being extended to include other metal ions such as  $\text{Na}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Fe}^{3+}$  in addition to  $\text{Ca}^{2+}$ . At certain concentrations of  $\text{Ca}^{2+}$  and pH the plots of interfacial tension versus logarithmic bulk concentration of HDEHP are reminiscent of those for a surfactant forming aggregates in bulk solution. This phenomenon of aggregate formation is being examined by a low-angle laser light-scattering method. An interfacial rheometer is being constructed to study the interfacial viscosity of extractant films. Efforts presently are focused on mass transfer and distribution studies of the extraction of  $\text{Ca}^{2+}$  from aqueous solutions to a n-hexane phase by HDEHP. Attention is also directed toward examining the fine structure of interfacial films by electron microscopy.

**University of Missouri**  
**Rolla, Missouri 65401**

**384. An Extraction/Separation Process With Extreme Energy Efficiency**

*S. Friberg, P. Neogi, Dept. of Chemistry* **\$86,000**

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.

**University of Oklahoma**  
**Norman, Oklahoma 73019**

**385. A Study of Micellar-Enhanced Ultrafiltration**  
*J.F. Scamehorn, S.D. Christian, School of Chemical Engineering and Materials Science* **\$64,899**

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. Very little of the organic solute passes through the membrane, resulting in a fairly pure filtrate, and in the retentate solution being very concentrated in the solute. Cationic surfactants have been found to be superior to anionic or nonionic surfactants and, as a result, hexadecylpyridinium chloride is being used in this work. The model organic solute whose separation is being studied is tert-4-butylphenol. The accuracy of assuming that the filtrate and retentate are in equilibrium under expected operating conditions is being investigated. The severity of concentration polarization effects is being determined. Reductions in feed solute concentrations by a factor of 100 in the filtrate have been observed. Conditions to attain even further reductions are being sought.

**University of Tennessee**  
**Knoxville, Tennessee 37996-1600**

**386. Systematic and Structural Studies of Polymeric Extractants For the Separation and Recovery of Metal Ions**  
*S.D. Alexandratos, Dept. of Chemistry* **\$81,400**

The research is directed toward the synthesis and evaluation of polymer-supported extractants, with emphasis on the properties of the polymeric support. Focus is on the development of polymeric extractants that will be commercially feasible for large-scale applications to the recovery of strategically important metals and within nuclear waste reprocessing plants. The study is concerned with four major points: (1) to develop an economical synthesis of the polymer support; (2) to utilize polymers that display high chemical, mechanical, and radiation stability; (3) to develop polymers with macroscopic properties allowing for a rapid rate of metal ion complexation; and (4) to produce polymeric extractants with a high density of active sites in order to minimize bed volumes. The principle polymer support examined to date is polystyrene, in bead form, at various levels of crosslinker and macroporosity. Bonding phosphinic acid moieties to the styrenic network yields a polymer-supported extractant found to absorb large levels of transition metal ions from aqueous solutions even at low pH values. Sulfonic acid and carboxylic acid groups bonded to the styrenic network are also being studied. Introduction of a higher level of selectivity is accomplished by the synthesis of polymer networks supporting both (pseudo)crown ethers and a cation exchange group.

**387. Capillary Separations With Calorimetric Absorbance Detection**  
*M.J. Sepaniak, Dept. of Chemistry* **\$61,400**

The objective of this project is development and utilization of laser-based calorimetric absorbance detection techniques in microscale liquid chromatography. A single beam configuration has been employed for a preliminary evaluation of thermal lens detection in open tubular liquid chromatography. Nitroaniline compounds were efficiently separated on 20  $\mu\text{m}$  i.d. bonded-phase columns and detected with sensitivities that rival fluorometric detection. A more versatile pulsed double beam configura-

ration, exhibiting enhancements in sensitivity relative to Beer's Law of one-two orders of magnitude, was constructed. This thermal lens detector is being employed in the detection of nitropyrene compounds separated using  $\mu$ -bore liquid chromatography columns. Procedures for reliably preparing bonded-phase open tubular columns are under investigation. Very good chromatographic efficiencies have been obtained for separations using open tubular columns prepared from soda-lime and borosilicate glasses. In addition, dynamically modified open tubular columns are being investigated for bioseparations.

**University of Texas at El Paso**  
El Paso, Texas 79968-0513

**388. Macrocyclic Lanthanide Ion Selective Reagents**  
C.A. Chang, Dept. of Chemistry \$50,000

This research involves a topological approach for the design, synthesis, and characterization of macrocyclic lanthanide ion selective reagents. Macrocyclic aza-crown ethers, with pendent ionizable groups and a variety of structural features, are being prepared. Fundamental studies of their lanthanide complexes concerning thermodynamic and kinetic stabilities, solution and solid state structures, as well as the solvent extraction and liquid chromatographic behavior are being performed. Factors such as (1) the cavity size, and (2) the stereochemical constraint of the reagents are being examined to correlate to the selective complexation of lanthanide ions. Comparative complexation studies using other metal ions are also under way for eventual practical applications (e.g., to nuclear fuel and waste processing and the recovery of strategic metals).

**University of Utah**  
Salt Lake City, Utah 84112

**389. Fourier Transform Photoacoustic Spectroscopy**  
E.M. Eyring, Dept. of Chemistry \$75,000

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. Numbered 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 plus 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 will be carried out over an extended range of temperatures and pressures. The objective will be the determination of the basic chemistry required for FT-IR/PBD spectroscopy to surpass FT-IR/PAS in usefulness. A byproduct of the resulting infrared spectral information will be an improved understanding of doping of semiconducting organic polymers. Some of the same polymer samples will be reexamined by PTR using pulses of near infrared radiation from a Raman shifted Nd:YAG laser to excite the sample and HgCdTe detectors to measure emitted radiation.

**390. Hydrophobic Character of Nonsulfide Mineral Surfaces As Influenced By Double Bond Reactions of Adsorbed Unsaturated Collector Species**  
J.D. Miller, Dept. of Metallurgy \$75,000  
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 have a significant effect on flotation rate and the hydrophobic character of non-sulfide minerals. Bubble attachment measurements indicate that attachment times decrease by an order of magnitude at higher temperature and higher oxygen partial pressure when compared to ambient conditions. These results suggest interaction of unsaturated chemisorbed carboxylate species, which may involve oxidation of the double bond and subsequent cross linking between adjacent unsaturated chains. The hydrophobic character of such surfaces is being studied by collector adsorption density measurements, microcalorimetric studies, and *in situ* FTIR spectroscopy. *In situ* spectroscopic experiments are being performed to identify the surface reaction product and establish whether or not oxidation of the double bond and polymerization of the chemisorbed species occurs at non-sulfide mineral surfaces. 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

**391. Glow Discharge As An Atomization and Ionization Source**  
W.W. Harrison, Dept. of Chemistry \$64,899

This project centers about the study of a glow discharge as an atomization and ionization source for trace element analysis of solids and solutions. Coupling of the glow discharge to a quadrupole mass filter results in a simple mass spectrometer system of considerable versatility. A variable duty pulsed discharge is being studied, and shows advantages over direct current operation. The use of short, high intensity pulses produces enhanced sputter action and a greater ion yield. Time-resolved selection of ions generated only during the trailing pulse edge produces a strong atomic signal for the cathode sample with discrimination against background gases. The use of laser enhanced ionization within the glow discharge is also under investigation. Resonance transitions stimulated by tuned radiation from an excimer/dye laser permit selective ionization of sputtered metal atoms. Up to 100% of the selected atoms in a given microvolume can be ionized for subsequent mass spectral analysis.

**University of Wyoming**  
Laramie, Wyoming 82071

**392. Solid Surface Luminescence Analysis**  
R.J. Hurtubise, Dept. of Chemistry \$77,400

The goal of this project is to develop a fundamental understanding of the physical and chemical interactions that induce strong room-temperature fluorescence and phosphorescence from organic compounds adsorbed on solid surfaces. Reflectance, infrared, and luminescence spectroscopy are being used to clar-

ify the interactions. The effects of moisture, several gases, and temperature on the luminescence quantum efficiencies and the phosphorescent lifetimes of adsorbed compounds are being investigated. The various experiments will help to determine if the luminescent molecules are being held rigidly, or if the solid matrix is preventing collisions with oxygen and water molecules. Basic and nonbasic nitrogen heterocycles, and hydroxyl aromatics are being used as model compounds to develop total luminescence derivative spectroscopy as a new approach in organic trace analysis. In addition, cyclodextrins are being used to induce room-temperature luminescence from adsorbed compounds. Finally, solid-surface luminescence is being employed to study interactions in adsorption chromatography.

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

**393. *Studies of the Analyte-Carrier Interface in Multicomponent Flow Injection Analysis***  
*S.D. Brown, Dept. of Chemistry* **\$75,000**

The use of flowing carrier solutions to transport injected analytes to a detector has received considerable attention recently. Situations where the injected analyte reacts with reagents present in the carrier have received almost no study, on the other hand. Analyte-carrier reagent interactions are controlled by several factors. Among these are dispersion of analytes and carrier solutions, reaction kinetics of carrier reagents with components of the analyte solution, and the relative availability of reactants at the analyte-carrier reagent interface. This project involves the study of product distributions at the analyte-carrier reagent interface as a function of dispersion, reaction kinetics, and local stoichiometric effects. For these studies, a rapid-scan electrochemical flow detector is used to obtain "maps" of reaction product distributions at the analyte-carrier reagent interface. The added information obtained in probes of these distributions is useful in the design of species-specific analyses and multicomponent analyses using flowing solutions.

**Chemical Engineering Sciences**

**Brigham Young University**  
Provo, Utah 84602

**394. *Thermodynamic Study of CO<sub>2</sub>-Organic Compound Interaction At High Pressures and Temperatures***  
*R.M. Izatt, J.J. Christensen, Dept. of Chemical Engineering* **\$71,900**

The primary objective of this project is to gain increased knowledge of the energetics associated with the interaction of CO<sub>2</sub> and Freons with selected organic compounds under temperature-pressure conditions where either one or more of the components is in its super-critical region. The quantities measured include heats of mixing of binary and ternary mixtures and constant pressure heat capacities of pure components and of mixtures. The temperature and pressure ranges covered are 285-673 K and 8-12.5 MPa, respectively. Flow calorimeters will be used to obtain the experimental data. The data will be incorporated into equations which will describe the variation of each quantity over

the temperature and pressure ranges studied. The eventual goal is to elucidate the chemistry occurring when supercritical fluids are involved in solvent extraction processes.

**California Institute of Technology**  
Pasadena, California 91125

**395. *Dynamics of Vapor Explosions***  
*B. Sturtevant, Graduate Aeronautical Laboratories* **\$46,000**

The effect of ambient pressure on the baroclinic interfacial instability of rapid vaporization has been studied experimentally and theoretically in single droplets boiling explosively at the limit of superheat. In a series of experiments with pentane, isopentane, and ethyl ether in a bubble-column apparatus it has been shown that the instability of super-heat-limit boiling may be suppressed by increasing the ambient pressure. While at atmospheric pressure bubble boundaries are rough and opaque due to small-scale instability-generated distortions, at elevated pressure the liquid-vapor interface is smooth and transparent. The radiated pressure field is two orders of magnitude smaller from stabilized bubbles than from unstable. In the stable boiling regime the largest radiated pressures are a consequence, not of boiling, but of violent bubble oscillations that occur after the droplet has completely vaporized. At intermediate pressures bubble growth occurs in two stages, first stable, then unstable. The Landau mechanism for the instability of laminar flames has been adapted to the case of vaporization by accounting for the effects of surface tension and acceleration. A formulation of the theory in spherical geometry predicts absolute stability at atmospheric pressure, while the theory for planar interfaces yields results in accord with observation. Apparently, the instability occurs at such small wavelengths that the spherical constraint is inappropriate.

**City College of New York**  
New York, New York 10031

**396. *Turbulence and the Distortion of Reactions***  
*J.A. Johnson, Dept. of Physics* **\$80,000**

Contact surfaces in a pressure-driven shock tube are used as a way of investigating the possibility of the manipulation of molecular recombinations. Turbulent bursts are produced. The reaction  $2\text{NO}_2 + \text{X} \rightarrow \text{N}_2\text{O}_4 + \text{X}$  ( $\text{X} = \text{N}_2$  or  $\text{Ar}$ ) is unstable under some circumstances; fluctuations with amplitude incoherence and phase coherence are developed. Here, the use of standard reaction rate data proves to be inadequate. The point-resolved histories of density, velocity, and other flow and mixture properties are determined, using cross-beam correlations and fluorescence of NO<sub>2</sub> probed by the 4.88 nm line from an Ar<sup>+</sup> ion laser. The importance of the dynamical parameters of turbulence is being measured; specifically, the impact of changing local viscosity, characteristic turbulence scale, and turbulence intensity. In addition, there is some evidence that a reduced molecular chaos may be relevant to this kind of process. This possibility is given a quantitative formulation and tested in our data.

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

- 397. Interaction of Turbulence and Chemical Reactions**  
*R. Chevray, Dept. of Mechanical Engineering* **\$85,000**

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 ( $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2^* + \text{O}_2 \rightarrow \text{NO}_2 + \text{h}\Phi + \text{O}_2$ ). Large Reynolds numbers, small dilution numbers, large reaction speed numbers, and several concentration ratios 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 absorption spectroscopy, respectively. Simultaneous cine-film recording is conducted, in order 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 14853-0294

- 398. Experimental and Theoretical Studies of Dense Fluid Mixtures**  
*W.B. Streett, K.E. Gubbins, School of Chemical Engineering* **\$180,000**  
(24 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. Experimental research in progress includes measurements of the PVT properties of  $\text{CF}_4$  and  $\text{CHF}_3$  at pressures to 1000 bars. The direct-weighing PVT apparatus, designed and built under this project, has been completely redesigned and reconstructed to extend the temperature and pressure ranges to 0-600 C and 0-2000 bars, respectively. Measurements of the velocity of sound in fluids over wide ranges of pressure and temperature will be initiated in 1984-1985. Theoretical work has included development of statistical mechanical methods for calculating the effects of molecular polarizability, including complicated multibody induction effects. These effects have been found to be almost an order of magnitude larger than anticipated on the basis of dilute gas calculations.

**Hokenson Company**  
Los Angeles, California 90005

- 399. Coherent Structure: Reflective Turbulence Modeling of Complex Shear Flows**  
*G.J. Hokenson, Fluid Mechanics and Heat/Mass Transfer Division* **\$20,000**

The limitations of turbulence modeling with respect to the accurate prediction of complex shear flows will be analyzed. The flowfield effects of interest are associated with combustor flows and include strong: (1) pressure gradients; (2) streamline curva-

tures; and (3) density gradients. Each effect will be considered alone and in combination with others to isolate the modeling implications regarding: (1) basic turbulent structures; (2) gradient transport; and (3) isotropy. Of particular interest is the strong turbulence suppression or enhancement which each effect may induce, involving the possible generation of dispersive wave-like features with a corresponding non-diffusive and highly anisotropic nature. The project objective is to provide a framework for future research in which successful turbulence modeling prescriptions may be carried over to a multiple-fluctuating-element representation of the flow. In such a formulation, the physics of processes occurring at various scales and coherences may be differentiated from each other and depicted in a manner faithful to the experimental data. The practical utility of such an approach in providing accurate predictions of untested flows would then be tested.

**Johns Hopkins University**  
Baltimore, Maryland 21218

- 400. Prediction of Thermodynamic Properties of Coal Derivatives**  
*M.D. Donohue, Dept. of Chemical Engineering* **\$81,000**

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 multi-pole 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 being taken into account to predict properties of systems containing  $\text{H}_2\text{O}$ , alcohol, and so forth. High pressure vapor-liquid equilibrium measurements for  $\text{CO}_2$ -aromatic binary mixtures are being made.

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

- 401. Experimental and Theoretical Study of the Thermophysical Properties of Fluid Mixtures**  
*H.J.M. Hanley, Fracture and Deformation Div.* **\$205,000**

The program combines experiment, theory, and correlation to study the properties and behavior of fluids. Specific objectives are to produce PVT and thermodynamic data on hydrocarbon fluids and their mixtures at high temperatures (to 900 K) and pressures (to 35 MPa, possibly to 100 MPa) so as to (1) develop the theory of liquids, and (2) develop models to predict the properties based on the theory and optimized by the data. PVT properties of  $\text{H}_2\text{S}$  and propane have been measured and correlated. Phase equilibria VLE measurements of the system  $\text{CO}_2$ /i-butane have been reported. Theoretical studies include computer simulation of fluids under shear for which several results have been published. A thermodynamics for a shearing system has been proposed. Predictions of shear induced phase

transitions in liquid/gas and liquid/liquid mixtures have been discussed. Plans include PVT studies of methanol and further computer simulation studies of mixtures.

- 402. Transport and Phase Equilibria in Multicomponent Fluids**  
J.M. Kincaid, Division of Thermophysics \$70,000

The purpose of this project is to develop and implement simple, accurate techniques to treat the transport and phase transition properties of multicomponent systems. There are three basic aspects to the project: (1) the development of new techniques to study multicomponent systems; (2) the translation and adaptation of recent theoretical advances in transport and phase transition phenomena to forms usable to the energy technologies; and (3) approximation assessment and implementation. All three of these areas can be expected to advance our understanding of multicomponent fluids at high temperatures. Recent progress includes: (1) the solution of several phase equilibria problems for polydisperse fluids; and (2) an analysis of molecular dynamics studies of diffusion in binary hard-sphere mixtures, which will be used to calibrate the revised Enskog theory.

**Purdue University**  
West Lafayette, Indiana 47907

- 403. Gas-Liquid-Liquid Equilibria in Mixtures of Water, Light Gases, and Hydrocarbons**  
K.C. Chao, H.M. Lin, School of Chemical Engineering \$75,000

Phase equilibrium in mixtures of water + light gases, and water + heavy hydrocarbons will be investigated in light of recent advances of group contribution, equation of state, and local composition. Toward the development of quantitative models of water solutions, experimental study will be made of gas-liquid equilibrium at temperatures up to 430°C and pressures to 300 atm, and of liquid-liquid equilibrium at temperatures up to 250°C.

**Stanford University**  
Stanford, California 94305

- 404. Transport Characteristics of Slurries in Pipelines: Flow Regimes and Pressure Drop**  
A. Acrivos, Dept. of Chemical Engineering \$0  
(No Fund Extension)

This research aims to study the flow of slurries in pipelines from a fundamental point of view. Primary emphasis is on developing methods, based on sound scientific principles, for predicting the pressure drop, and for delineating the various flow regimes that can occur in such systems. The theoretical framework is based on the equations of continuum mechanics, and is being developed in close conjunction with a parallel experimental study. A theoretical model is currently being developed to explain quantitatively the curious phenomenon whereby a settled suspension has been observed to resuspend in the presence of a laminar shear flow under conditions of very small Reynolds numbers. It is believed that resuspension is due to the action of a shear-induced diffusion of particles, and attempts currently are being made to measure the corresponding diffusion coefficient. The possible

connection between the shear-induced diffusion and the measured normal stresses in the suspension is being investigated.

- 405. Fundamental Studies of Heat Transport, Fluid Mechanics, and Stability in Porous Media**  
G.M. Homsy, Dept. of Chemical Engineering \$84,800

This program treats problems in flow and transport phenomena in porous media whose solutions are of interest in energy recovery processes. Broad categories of activities include macroscopic and microscopic descriptions. Regarding the former, theoretical and experimental studies of the effect of graded mobility on instabilities of displacement fronts have continued. The theory is being extended to study important effects of flow-induced dispersion, and adsorption loss of the mobility control agent. Experiments in a Hele-Shaw cell are continuing, and to date have shown the stabilization of displacements due to mobility gradation. A theory of finite-amplitude thermally driven instabilities in bounded porous regions has been completed, which determines the form of convection which will be observed. Microscopic studies of two phase Hele-Shaw flows have been completed with good agreement between theory and experiment. Microscopic modeling of non-Newtonian flow in porous media has been studied, indicating that constitutive equations of the Oldroyd type are incapable of capturing the salient experimental features of these flows. New studies of blob dynamics in constricted-tube models of porous media have begun.

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

- 406. Transport Properties of Multiphase Systems**  
G.R. Stell, Dept. of Mechanical Engineering \$165,000  
(24 mo.)

Ongoing research continues on the microscopic theory relating transport and structure in two-phase media, including new results on expected surface area, and on quantitative comparisons of bounds and approximations that involve two-particle and three-particle correlations in such media. Research also continues on new statistical mechanical theories of transport at both liquid-state and gaseous-state densities. The liquid-state work includes the use of an entropy-maximization technique as well as a molecular theory of solutions and suspensions. Both approaches lead to new quantitatively useful approximations for transport coefficients in the liquid state. The gaseous-state work includes the development of analytically tractable kinetic perturbation theories for useful model potentials. A kinetic approach to the theory of mixtures of interacting n-mers has yielded new, exact results in the description of the gelation point, and the post-gelation period for models that include and go beyond that of the Flory-Stockmayer theory.

**University of California/Davis**  
Davis, California 95616

- 407. Statistical Modeling and Analysis of Chemically Reacting Turbulent Flows**  
H.A. Dwyer, W. Kollmann, Dept. of Mechanical Engineering \$145,000  
(24 mo.)

This research program is directed toward development of new turbulent closure models for variable density turbulent flow and

turbulent diffusion flames. The methods utilized to accomplish these goals are (1) physical and mathematical modeling, and (2) sensitivity analysis. The modeling techniques cover the closure of density-velocity statistical correlations and the use of Monte Carlo simulations for scalar transport. The research has centered on turbulent jets, but a new effort on boundary layer flows has been initiated. Sensitivity analysis studies have been extended to variable density and combustion flows; the results are giving insight into the complex interaction between combustion and turbulent flow.

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

**408. Reaction Enhancement of Heterogeneously Catalyzed Reactions By Concentration Forcing**  
*R.G. Rinker, Dept. of Chemical and Nuclear Engineering* **\$57,800**

An investigation is under way to examine experimentally the underlying phenomena leading to enhancement of heterogeneously catalyzed reaction systems by periodic concentration cycling of reactants (concentration forcing). Several consequences of periodic cycling, compared to conventional steady-state operation for reactions with nonlinear pathways, include (1) higher time-averaged product yields, (2) longer catalyst life, (3) improved catalytic selectivity, and (4) lower energy costs. The results of this study, which is focusing on the synthesis reactions of ammonia and menthanol, are 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 rate-limiting step(s) in the overall conversion. The results are also expected to provide new directions for catalyst design. Kinetic and thermodynamic parameters of the selected reactions, for use in modeling unsteady-state operation, are obtained in a differentially-operated fixed-bed reactor by transient experiments capable of distinguishing among individual phenomenological steps. Mathematical simulations of integral fixed-bed reactors having plug flow or perfect mixing in the fluid phase and operated under periodic cycling conditions (either isothermally or adiabatically) are being used to compare alternate inlet conditions including pulse widths, frequencies, and compositions. Results of the simulations are being compared to the experiment.

**University of Pennsylvania**  
**Philadelphia, Pennsylvania 19104**

**409. Thermodynamics of Systems of Very Many Components**  
*E.D. Glandt, Dept. of Chemical Engineering* **\$79,900**

The purpose of this research is to develop a quantitative description of fluid mixtures of very many components by using a continuous distribution of an arbitrarily chosen parameter. The continuous or polydisperse Lennard-Jones fluid, where the molecular parameter is the distributed variable, is being studied first since it is an appropriate representation of hydrocarbon systems. The thermodynamic properties of this model mixture are studied by two complementary approaches: (1) Monte Carlo computer simulations; and (2) perturbation theory. In the perturbation theory calculations the reference fluid is the pure most

abundant component while the small, perturbing parameter is the second moment or "width" of the composition distribution function.

**University of Washington**  
**Seattle, Washington 98195**

**410. Experimental Determination of the Mixing Frequency Parameter For Coalescence/Dispersion Modeling of Turbulent Combustion**  
*G.W. Butler, Dept. of Mechanical Engineering* **\$70,000**

The purpose of this experimental study is to advance the understanding of the physics and physical modeling of turbulent mixing in high intensity combustion. Specific objectives of this research are: (1) to measure the characteristic fluid-mixing frequency in a jet-stirred reactor over a range of practical fuel-air equivalence ratios using time-resolved stimulus-response techniques; (2) to compare the experimental data with existing analytical and numerical models for combustor mixing frequencies which are derived from global fluid mechanical arguments; and (3) to interpret the measurements in order to model the dependence of the characteristic mixing frequency on the physical parameters of the high intensity combustion. From this study, physically based models of turbulent mixing frequencies which characterize high intensity combustion are expected. It is furthermore anticipated that these models will be used to extend the predictive and potential design utility of numerical coalescence/dispersion modeling of turbulent combustion processes.

## FY 1984 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.) Chemical Sciences FY 1984 equipment funds were assigned as follows:

<b>Facility</b>	<b>Equipment funds</b>
Ames Laboratory	447,000
Argonne National Laboratory	1,105,000
Bartlesville Energy Technology Center	15,000
Brookhaven National Laboratory	1,491,000

<b>Facility</b>	<b>Equipment funds</b>
Idaho National Engineering Laboratory	11,000
Lawrence Berkeley Laboratory	1,071,000
Lawrence Livermore National Laboratory	0
Los Alamos National Laboratory	64,000
Mound Facility	71,000
Notre Dame Radiation Laboratory	252,000
Oak Ridge National Laboratory	691,000
Pacific Northwest Laboratory	116,000
Pittsburgh Energy Technology Center	7,000
Sandia National Laboratories, Albuquerque	58,000
Sandia National Laboratories, Livermore	800,000
Solar Energy Research Institute	65,000

## 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 in-house staff members.

Each of the facility summaries also gives the names of individuals to contact for further information, a general description of the facility, and a list of technical data on the primary available instrumentation.

The Office of Basic Energy Sciences also supports other facilities not summarized here. Information concerning these can be obtained by contacting Dr. Louis C. Ianniello, Director of Materials Sciences, ER-13, U. S. Department of Energy, Washington, D.C. 20545.

Chemistry Division  
Argonne National Laboratory  
Argonne, Illinois 60439

## ATOMIC SPECTROSCOPY FACILITY

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, high-temperature furnaces for metal-vapor absorption tubes, and an automatic plate-measuring comparator. YAG-laser-driven dye lasers are used with doublers and H<sub>2</sub>-Raman scattering to cover the 2500- to 8500-Å range and to produce coherent radiation between 1180 and 1250 Å by four-wave mixing in mercury vapor at fluxes ranging from 10<sup>10</sup> to 10<sup>16</sup> photons/sec for resolving powers of several million. The experimental work is reinforced by extensive computational programs for interpreting line broadening, diamagnetic, and hyperfine structure data in terms of fundamental atomic theories.

### COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists.

### PERSON TO CONTACT FOR INFORMATION

J. P. Hessler  
Chemistry Division  
Argonne National Laboratory  
9700 South Cass Avenue  
Argonne, Illinois 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, Å	
30-foot Paschen-Runge spectrograph	2000 to 9000
5-meter Czerny-Turner spectrograph	1200 to 9000
Tunable dye lasers	2500 to 8500
Vacuum-ultraviolet coherent source	1180 to 1250

Physics Division  
Argonne National Laboratory  
Argonne, Illinois 60439

## 4.5-MV DYNAMITRON ACCELERATOR

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 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 spectroscopy setup with associated high-resolution photon (optical and X-ray) spectrometers, (3) a 28-inch-diameter general-purpose scattering chamber, (4) a simultaneous irradiation system by which ion beams from the Dynamitron and from a 2-MV Van de Graaff accelerator are focused onto the same target, (5) a variety of electron spectrometers including a high-resolution, large solid-angle McPherson spherical analyzer, and (6) 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 PDP-11/45 computer system with a direct link 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.

Chemistry Division  
Argonne National Laboratory  
Argonne, Illinois 60439

## PREMIUM COAL SAMPLE PROGRAM

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 will be as chemically and physically identical as possible, will have well-characterized chemical and physical properties, and will be stable over long periods of time. Coals will be 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

Initial samples are expected to be available in early 1984. Samples will be made available to research personnel at a

### PERSON TO CONTACT FOR INFORMATION

D. S. Gemmell  
Physics Division  
Argonne National Laboratory  
9700 South Cass Avenue  
Argonne, Illinois 60439

Phone:  
Comm. (312) 972-4004  
or FTS 972-4004

### TECHNICAL DATA

Range of terminal voltages attainable	0.3 to 4.5 MV
Range of ion beam currents attainable	0.1 nA to 100 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

nominal replacement cost. A very limited quantity of lump coal, stored under similar inert conditions, will be available on special request for special physical property measurements. Distribution of these samples will be guided by policies established with the help of a users advisory committee. The processing facility may be available for occasional processing of special samples.

### PERSON TO CONTACT FOR INFORMATION

Dr. Karl S. Vorres  
Chemistry Division, Bldg. 200  
Argonne National Laboratory  
9700 South Cass Avenue  
Argonne, Illinois 60439

Phone:  
Comm. (312) 972-7374  
or FTS 972-7374  
Telex:  
TWX 910-258-3285  
USDOE-CH ARGN

Chemistry Division  
Argonne National Laboratory  
Argonne, Illinois 60439

## PULSE RADIOLYSIS FACILITY

The Argonne linear electron accelerator was designed for chemical research. The moderate energy of the electron accelerator (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 liquids, transient concentrations up to 20  $\mu$ M can be generated with the 25-psec pulse, and concentrations in excess of 10 mM can be generated with the longest pulse. Instrumentation for measurement of chemical processes allows kinetic spectrophotometric absorption and emission and fast conductivity measurements. Simultaneous multiwavelength kinetic spectrophotometric measurements are possible, and very high time resolution measurements that use the short pulse capability of the linac can also be made, both in absorption and emission. Other detection techniques, such as resonance Raman spectroscopy, are under development. 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.

National Synchrotron Light Source  
Brookhaven National Laboratory  
Upton, New York 11973

## NATIONAL SYNCHROTRON LIGHT SOURCE

The National Synchrotron Light Source (NSLS) facility consists of a 750-MeV (9-electron bunch) storage ring for VUV and IR research and a 2.5-GeV (30-electron bunch) 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. A 6-pole superconducting wiggler magnet and a 38-pole permanent magnet undulator have been constructed, and several 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 will be used by biologists, chemists, solid state physicists, metallurgists, and engineers for basic and applied

### PERSON TO CONTACT FOR INFORMATION

Charles D. Jonah  
Chemistry Division  
Argonne National Laboratory  
9700 South Cass Avenue  
Argonne, Illinois 60439

Phone:  
Comm. (312) 972-3471  
or FTS 972-3471

### TECHNICAL DATA

Energy	
Transient mode	21 MeV
Steady-state mode	14 MeV
Pulse repetition rate	Single pulse, 800 pps (800 pps not possible for all pulses)
Current/pulse	
Transient mode	20 A
Steady-state mode	1.5 A
Picosecond pulse	25 nC
Pulse width	30 psec 4 to 100 nsec 0.25 to 10 $\mu$ sec

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, 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 are being 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.

General Users will be able to perform experiments on an NSLS facility beam line or on a PRT beam line, which will

be available for use by non-PRT members for at least 25% of its total operational time. For the PRT beam line, PRT's will provide liaison and utilization support to General Users. After an initial commissioning period, NSLS and PRT beam lines will become available for use by 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 limited amount of funding will be available to scientists from U. S. institutions of higher education under the NSLS-HFBR Faculty/Student Support Program. The program is designed to defray expenses incurred by faculty/student research groups performing experiments at the NSLS or at the HFBR. It is aimed at university users having only limited grant support for their research and will be used to support only the most deserving cases.

### PERSON TO CONTACT FOR INFORMATION

R. Klaffky	Phone:
NSLS, Bldg. 510E	Comm. (516) 282-4974
Brookhaven National Laboratory	or FTS 666-4974
Upton, New York 11973	

### TECHNICAL DATA

Facilities	Key features	Operating characteristics
VUV electron storage ring	High brightness; continuous wavelength range ( $\lambda > 5 \text{ \AA}$ ); 16 beam ports	0.75-GeV electron energy
X-ray electron storage ring	High brightness; continuous wavelength range ( $\lambda > 0.5 \text{ \AA}$ ); 28 beam ports	2.5-GeV electron energy

Instruments	Key features
Monochromators	
Plane grating	$12 \text{ \AA} < \lambda < 1500 \text{ \AA}$ ; high resolution
Zone plate	$8 \text{ \AA} < \lambda < 100 \text{ \AA}$ ; moderate resolution
Toroidal grating	$10 \text{ \AA} < \lambda < 2500 \text{ \AA}$ ; high intensity; moderate and high resolution
Extended range grasshopper	$20 \text{ \AA} < \lambda < 2000 \text{ \AA}$ ; high resolution
Wadsworth	$300 \text{ \AA} < \lambda < 3000 \text{ \AA}$ ; high intensity; moderate resolution
Seya and Czerny-Turner	$1200 \text{ \AA} < \lambda < 12000 \text{ \AA}$ ; high intensity; moderate resolution
Two crystal	$0.04 \text{ \AA} < \lambda < 2500 \text{ \AA}$ ; high resolution; fixed exit beam
Two crystal/two grating	$2.5 \text{ \AA} < \lambda < 2500 \text{ \AA}$ ; 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
Superconducting wiggler	$\lambda > 0.1 \text{ \AA}$ ; high intensity
Permanent magnet undulator	$100 \text{ \AA} < \lambda < 1000 \text{ \AA}$ ; high intensity and brightness

Department of Physics  
Kansas State University  
Manhattan, Kansas 66506

## JAMES R. MCDONALD LABORATORY

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) 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, and (6) 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. McDonald Laboratory  
Department of Physics  
Kansas State University  
Manhattan, Kansas 66506

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

## PULSE RADIOLYSIS FACILITY

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 ~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.

## 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:  $ME/q^2 \leq 150$

### 3-MV Van de Graaff

Beams:  $^1H$  or  $^4He$   
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

### COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists or by a proposal to the laboratory director.

### PERSON TO CONTACT FOR INFORMATION

R. H. Schuler, Director                      Phone:  
Notre Dame Radiation Laboratory      Comm. (219) 239-7502  
Notre Dame, Indiana 46556              or FTS 333-8222

## TECHNICAL DATA

Electron source	8-MeV linear accelerator
Operating mode	Single pulse, with signal averaging
Data collection	PDP-8
Pulse width	5, 10, 20, 50 nsec
Time resolution (RC)	2 nsec
Pulse current	Up to 1 A
Repetition frequency	0.2 sec <sup>-1</sup>

Operations Division  
Oak Ridge National Laboratory  
Oak Ridge, Tennessee 37830

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

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. An important aspect of the program is the research, development, and demonstration of cost-effective alternate methods of isotope enrichment as well as activities in ion source technology, beam dynamics, ion retention, 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

Physics Division  
Oak Ridge National Laboratory  
Oak Ridge, Tennessee 37831

of the material in the Research Materials Collection. Applications for the loan of samples from this collection for non-destructive research projects germane to DOE programmatic interests are received at any time.

### PERSON TO CONTACT FOR INFORMATION

E. Newman, Head	Phone:
Isotopes Section	Comm. (615) 574-4846
Operations Division	or FTS 624-4846
Oak Ridge National Laboratory	
P.O. Box X	
Oak Ridge, Tennessee 37831	

## EN-TANDEM

The EN-Tandem is operated primarily as an atomic physics facility. The highest terminal voltage is 6.5 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 position sources (being developed).

### 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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### TECHNICAL DATA

Beams: Most elements  
Terminal voltages: 0.3 to 6.5 MV  
Source beam currents: Several hundred nA to several  $\mu$ A  
Output currents: Up to 1  $\mu$ A, depending on the ion species and charge state  
Repetition rate: DC only (at present)  
Magnet limitations:  $ME/q^2 \leq 80$

Operations Division  
Oak Ridge National Laboratory  
Oak Ridge, Tennessee 37830

## HIGH FLUX ISOTOPE REACTOR

The prime purpose of the High Flux Isotope Reactor (HFIR) is to make research quantities of  $^{252}\text{Cf}$  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/( $\text{cm}^2 \cdot \text{sec}$ ) is available to irradiate the curium target material. The HFIR is a beryllium-reflected light-water-cooled and -moderated, flux-trap reactor with a design power level of 100 MW. It burns 93% enriched  $^{235}\text{U}$  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/( $\text{cm}^2 \cdot \text{sec}$ ). These facilities can accommodate static experimental capsules, complex fuel-testing engineering loops, and special experimental isotope irradiations, the targets for which are prepared by the Oak Ridge National Laboratory Isotopes Group. Four beam tubes are used for neutron-diffraction experiments and a small-angle neutron scattering facility sponsored by the National Science Foundation is available for use by researchers from universities, industry, and other national laboratories.

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Chemical Technology Division  
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## TRANSURANIUM PROCESSING PLANT

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  $^{257}\text{Fm}$ . 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 nation-

ally 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.

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Combustion Sciences Directorate  
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 Livermore, California 94550

## COMBUSTION RESEARCH FACILITY

Current activities at the Combustion Research Facility (CRF) supported by the Division of Chemical Sciences emphasize the development and the applications of new diagnostic techniques to the study of basic flame processes, as well as *research in fundamental chemistry important in combustion*. (These programs are individually described elsewhere in this publication). In addition, DOE/Conservation sponsors programs at the CRF in combustion technologies, and DOE/Fossil supports programs in coal combustion and related diagnostics development.

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.

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### TECHNICAL DATA

Equipment	Key features
Flashlamp-pumped, tunable dye laser	Long pulse, high energy, high average power: 2- $\mu$ sec pulse length 5 J/pulse, 10 Hz Tunable 440 to 620 nm 0.03-nm bandwidth
Multipurpose pulsed laser system	High peak power, high resolution doubled YAG and tunable dye lasers: Single mode capability 10 to 500 mJ/pulse 10 to 20 nsec/pulse
Low-pressure flames	10 $\mu$ to 1 atm Mass spectrometer sampling probe
Atmospheric flames	Diffusion and premixed flames
High-pressure flame	Combination of diffusion flame burner with high pressure flow chamber: Pressures up to 20 atm Slot-geometry burner 2-0 laminar diffusion
Vertical turbulent diffusion flame	Open-circuit, induced-draft wind tunnel with co-flowing axisymmetric fuel jet: 30- by 180-cm viewing section to 6000 scfm flow
Atmospheric Combustion Exhaust Simulator (ACES)	Atmospheric pressure combustion exhaust chamber: To 1200°C 0.5 to 100 m/sec flow speed Trace species and particulates Optical and physical probes Materials test section

<b>Equipment</b>	<b>Key features</b>	<b>Equipment</b>	<b>Key features</b>
Combustion bomb	Simulates constant-volume engine combustion		Laboratory for laser ionization, saturation, optogalvanic detection of trace species
Internal combustion research engines	Highly repeatable environment for homogeneous charge and diesel combustion studies		Kinetics laboratories with tunable quasi-cw UV and ring dye lasers for analysis; excimer lasers for photolysis
Experimental diagnostics research facilities	Laser fluorescence laboratory  Coherent Raman spectroscopy laboratories	Computing facilities	Minicomputers in laboratories Access to CRF VAX 11/780 Access to Sandia National Laboratory, Livermore, CRAY via in-house staff

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