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Summaries of FY 1987 Research in the Chemical Sciences

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

This report was compiled for the Office of Energy Research from project summaries contained in the Research-In-Progress (RIP) 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 provide information to those interested in research supported by the Department of Energy's Division of Chemical Sciences, which is one of six Divisions of the Office of Basic Energy Sciences in the Office of Energy Research. This publication includes projects supported by both the Chemical Sciences budget and that portion of the Nuclear Sciences budget which is administered by the Division of Chemical Sciences.

These summaries provide to members of the scientific and technical public, as well as 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 indicated in the section headings, the listing of "Selected Topics of General Interest," and the summaries themselves. Energy technologies that can be advanced by use of the basic knowledge generated in this program are provided in the "Selected Topics" list and are often referenced in the summaries themselves.

Chemists, physicists, chemical engineers, and others considering the possibility of proposing research for support will find the publication useful for gauging the scope of the present program in basic research and the relationship of their interests to the overall program. Proposals that expand this scope will also be considered or directed to more appropriate offices. The research summarized here is intended to add significantly to the knowledge base on which existing and future energy technologies can evolve. 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 emphasis on chemical, physical, and chemical engineering subdisciplines which are advancing in ways that produce new information related to energy.

The program takes place in several different kinds of performing organizations. About half the projects are at DOE laboratories and half at universities and industrial laboratories. In DOE laboratories, much of the research utilizes special unique facilities which, in some instances, are national user facilities.

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

Robert S. Marianelli, Director
Division of Chemical Sciences
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*On leave from Seton Hall University.

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

Fundamental Interactions Branch (KC-03-01-)

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

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

Chemical Physics (KC-03-01-02)

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

Special emphasis is placed on basic research related to combustion; spectroscopy, theory, and the kinetics of elementary combustion reactions are of special interest. A major user-oriented facility, the Combustion Research Facility (CRF) at Sandia Laboratories/ Livermore is supported by this program. This laboratory offers use of advanced instrumentation to interested combustion scientists from universities, industry, and national laboratories.

Atomic Physics (KC-03-01-03)

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

Processes and Techniques Branch (KC-03-02-)

Chemical Energy (KC-03-02-01)

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

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

The separations part of the program is directed toward improving our basic understanding of methods for separating mixtures of gases, liquids, solids, and their component molecules, cations, anions, and isotopes. The program covers a broad spectrum of separations concepts, including membrane processes, extraction at both standard and supercritical conditions, adsorption, chromatography, photodissociation, complexation, etc. The program is technique oriented rather than species oriented; i.e., the research involves elucidating fundamental chemical phenomena for improved separations rather than developing specific processes for the separation of a particular species from particular matrices. The isotope separation program emphasizes isotopic properties and isotope effects and is basic in nature.

The analysis part of the program is aimed at supporting research on analytical techniques where a better understanding of basic chemical phenomena may facilitate improvements in sensitivity, reliability, and ease of operation and/or lower the costs of analytical determinations. Entirely new analytical techniques are also investigated, although this program does not support instrument development. New techniques are quickly reported in the literature so that those interested in instrument development can build on work supported herein. The program is not geared to using existing techniques to unravel the composition of samples nor to developing techniques to analyze particular chemical species or sample types. Rather, it is aimed at obtaining a thorough understanding of the basic chemistry of an analytical technique so that others may use this understanding to improve its utility.

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

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

Isotope Preparations (KC-01-02)

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

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

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

Chemical Sciences Division

Stanford Synchrotron Radiation Laboratory (KC-01-03)

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

LABORATORY ADMINISTRATION

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

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SUMMARIES OF FY 1987 RESEARCH IN THE CHEMICAL SCIENCES

NATIONAL LABORATORIES

Photochemical and Radiation Sciences

Ames Laboratory
Iowa State University

Ames, Iowa 50011

Fundamental Interactions Program **$380,000**

1. *Photoinduced Electron-Transfer Reactions in Protein Matrices*

N.M. Kostić

The project objective is measurement of rates and elucidation of mechanisms of electron-transfer reactions similar to those involved in plant photosynthesis and in other processes for conversion of solar into chemical energy. Selective binding of transition-metal complexes to metalloproteins and cross-linking of metalloproteins with transition-metal complexes result in novel electron-transfer systems, in which intramolecular redox reactions can be effected over long distances, in protein environments whose structural and thermodynamic properties are determined by spectroscopic and electrochemical measurements. We are working to discern the following key factors that affect the rates of electron transfer: intersite distance, nature of the intervening medium, temperature, and thermodynamic driving force. A particularly novel aspect of this project is the possibility of comparing ground-state and excited-state electron-transfer reactions under similar conditions. [2.5 FTE]

2. *Laser Spectroscopy and Electronic Energy Transfer of Light Conversion Systems*

G.J. Small

This project focuses on (1) the relationships between structure, pigment–pigment and pigment–protein interactions, and the electronic excitation and electron transfer processes in photosynthetic antenna and reaction center (RC) complexes; and (2) the engineering of ultrafast unidirectional electronic excitation transfer over macroscopic distances. A variety of laser spectroscopies are used, including solid-state hole burning, four-wave mixing, and two-photon coherent excitation. The former two are used to study the excited-state electronic and vibrational structures of the RC of photosynthetic bacteria and photosystem I of green plants. Focus is on understanding the electron–protein coupling and its role in electron transport. In a parallel fashion, the nature and dynamics of excitation transport in the antenna complex, which directs excitation to the RC, are being investigated. [2.5 FTE]

3. *Picosecond Spectroscopy and Reaction Dynamics*

W.S. Struve

Picosecond fluorescence spectroscopy is used to study excited-state decay processes of organic molecules in disordered systems. Since a verifiably accurate theory has not yet been developed for excitation transport and trapping in two dimensions (i.e., on surfaces), we have been obtaining detailed fluorescence profiles for well-characterized dye coverages in Langmuir-Blodgett monolayers to assess the limitations of the present theory. We have also examined fluorescence decays and picosecond-resolved transient absorption of dyes adsorbed on semiconductors, and have found that dye-to-surface mode nonradiative decay is an extremely efficient process on single-crystal TiO_2 and ZnO. Thus, such nonradiative decay is a likely origin of low photocurrent yields in many liquid junction cells. We are studying time-resolved electron–hole recombination luminescence in CdS and CdSe crystallites, and will probe the kinetics of hot-electron relaxation in these small ($\leqslant$ 50 A diameter) semiconductor particles. Dispersive excitation transport is being investigated for porphyrin molecules in low-temperature glasses between 10 and 300 K, because dispersive effects are likely to become important in disordered systems with large site inhomogeneity. [2.5 FTE]

Argonne National Laboratory

Argonne, Illinois 60439

Chemistry Division **$5,400,000**

4. *Electron Transfer and Energy Conversion*

J.R. Miller, D. Meisel, K.H. Schmidt

This project examines chemical processes, especially electron-transfer processes, that can occur in assemblies of molecules to effect photochemical energy conversion and storage. Molecular assemblies may include an ordered series of electron donor/acceptor molecules, such as in natural photosynthetic reaction centers, particles of redox catalysts such as colloidal semiconductors, and combinations of these assemblies. Current research explores the fundamental chemistry of electron transfer between molecules and at the surfaces of colloidal particles. By using pulse radiolysis, it is possible to measure how the distance between two molecules affects the rate of electron transfer between them. These studies also examine how the rates are enhanced by "through-bond interactions," which occur when the molecules exchanging an electron are connected by a molecular "spacer" group, and effects of the relative orientations of the molecules. Electron transfer and proton uptake at the surface of semiconductor colloids are studied by photoexcitation of the semiconductor to produce electron–hole pairs. Pulse radiolysis is used to study the same processes, but often with clearer results, because electrons or holes can be added to the semiconductor particles rather than both at once. Corrosion chemistry of these types of colloidal semiconductors and electronic properties of the colloids, such as "quantum size effects," are also examined. Chemical reactions of actinide ions and their colloids are also investigated by pulse radiolysis, which merges our capabilities with those of the Heavy Elements Group. [10.3 FTE]

5. *Physicochemical Investigation of Photosynthesis*

J.R. Norris, M.K. Bowman, T.J. Michalski, J. Tang, M. Thurnauer, D. Tiede

The major concern of this project is the extraction of chemical work from sunlight. The structure of natural photoreaction centers and the primary fast chemistry and physics that occur during photosynthesis are studied in detail. Time-domain optical and magnetic resonance spectroscopies are used to measure distances, orientations, and dynamics within the molecular components that participate in the transfer of electrons. These spectroscopic studies are guided by structural information available from x-ray diffraction. Our extensive knowledge of bacterial photosynthesis is now being applied to the study of charge separation and electron transfer in green plants. New magnetic resonance methods and data processing theory are developed specifically to characterize ultrafast charge separation in artificial and natural chemical systems. The project objective is the ability to describe bacterial and green plant photosynthesis in sufficient detail for constructing artificial systems that will perform efficient photosynthesis in the laboratory. [7.4 FTE]

6. *Chlorophyll and Photosynthesis Research*

J.R. Norris, J.J. Katz, M.K. Bowman, T.J. Michalski

The project objective is to understand the function of chlorophyll in photosynthesis (i.e., in light collection and energy transfer and in charge separation). This understanding requires study of the basic physical and chemical properties of the chlorophylls. We are particularly interested in the coordination interactions of the chlorophylls because we believe that the self-assembled chlorophyll species formed by the expression of these forces are responsible for the characteristic features of *in vivo* antenna and reaction center chlorophyll. We are currently studying: (1) the structure and EPR properties of colloidal chlorophyll micelles, which we believe have some structural features similar to *in vivo* antenna chlorophyll; and (2) the synthesis and characterization of chlorophyll model systems intended to mimic some aspect of *in vivo* photoreaction centers and antenna chlorophyll. [2.4 FTE]

7. *Preparation of Organisms, Photosynthetic Pigments, and Biological Materials of Unusual Isotopic Composition*

D. Tiede, H.L. Crespi, J.R. Norris

The project objective is the production of photosynthetic and other microorganisms substituted with biologically important rare stable isotopes, such as ^{2}H, ^{13}C, ^{15}N, ^{17}O or ^{18}O, and ^{25}Mg. Large quantities of green algae, cyanobacteria, and photosynthetic bacteria are routinely available in unnatural isotopic composition involving single or multiple isotope substitutions. These unusual organisms (and the compounds obtained from them) have significant applications in electron paramagnetic and nuclear magnetic resonance studies of photosynthesis and of protein structure, small-angle neutron scattering studies of multicomponent biological systems, and resonance Raman spectroscopy of bacteriorhodopsin. Of particular relevance is the ability to provide ^{2}H-bacterial reaction centers containing a double ^{1}H–amino acid enrichment for proton magnetic resonance spectroscopy. Genetically engineered bacteria are also cultured to give good yields of the protein of the cloned gene. [0.9 FTE]

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

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

This project studies the chemical consequences of interactions of ionizing radiation with matter. The goal is to describe the transformation of particle kinetic energy or photon energy into chemical energy, as expressed in chemical reactions and very short-lived chemical species. The ultrafast phenomena associated with this transformation are studied in real time with state-of-the-art tools, including the high-current electron linac (which now can give 5-ps pulses), a pulsed electron Van de Graaff accelerator, a picosecond ultraviolet laser, and associated time-resolved optical and magnetic resonance detection apparatus. Focus is on studying the chemical reactivity of short-lived intermediates in the liquid and solid states. The aim is to identify, to determine the structure, and to learn about the dynamics of unstable intermediates important in radiation chemistry and photochemistry in polar and nonpolar liquids and solids. The chemical consequences of excess energy excitation in neutral, charged, and paramagnetic intermediates are being examined. The role of solvation on the reactivity of the highly charged species, the solvated electron, is analyzed experimentally and theoretically. Rates of gas-phase reactions of radicals important in atmospheric and combustion chemistry are being determined. Pulse radiolysis methods allow measurements to be conducted at higher ($>$ 800 K) temperatures. [17.8 FTE]

9. *Artificial Photosynthesis*

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

The aim of this research is to synthesize and study molecular assemblies that mimic the primary events of photosynthetic energy conversion and storage. Studies of these biomimetic molecular assemblies are integrated with studies of natural photosynthetic reaction center proteins in order to develop a complete picture of the primary events of photosynthesis. The molecular assemblies consist of energy and/or electron donor and acceptor molecules that are positioned at known distances and orientations relative to one another. The dependence of ultrafast photoinduced energy- and electron-transfer rates on both the physical and electronic structure of these assemblies is probed with a variety of advanced spectroscopic techniques such as picosecond spectroscopy and time-domain magnetic resonance. [3.9 FTE]

Brookhaven National Laboratory
Upton, Long Island, New York 11973

Department of Applied Science $982,000

10. *Porphyrin Chemistry*
J. Fajer

This project addresses the role of porphyrin derivatives in bioenergetic reactions with particular emphasis on the mechanisms by which light is harvested and converted into chemical energy by chlorophylls in photosynthesis. The extensive body of data acquired to date for chlorophylls is equally applicable and relevant to the chemistry of the broad class of porphyrins and, in particular, to their functions in catalyzing nitrogen assimilation, hydroxylations, and carbon dioxide conversion. The work thus also seeks to exploit the chemistry of the recently discovered compounds of iron, cobalt, and nickel chlorins, isobacteriochlorins, and corphines that mediate these reactions. The project combines theoretical and experimental techniques to predict, identify, and characterize transients and mechanisms in these catalytic conversions. Experimental methods include photochemistry spectroelectrochemistry, magnetic resonance (ESR, ENDOR, and NMR), x-ray diffraction, and synchrotron radiation (EXAFS and edge studies), and are closely supported by several theoretical methods (SCF-MO-PPP, IEH, and INDO). Focus is on (1) structural consequences of electron transfer, (2) manganese chemistry in photosynthetic oxygen evolution, (3) nickel porphyrin chemistry relevant to the conversion of CO_2 to methane, and (4) variations in the macrocycles and their environment that control the chemistry of porphyrin-mediated bioreactions. [6.5 FTE]

11. *Electrochemistry and Photoelectrochemistry*
S. Feldberg

The project objective is fundamental understanding of a variety of electrochemical and photoelectrochemical phenomena. Areas of interest comprise a mixture of experimental and theoretical investigations and involve a number of collaborations outside Brookhaven National Laboratory. The major experimental effort deals with the development and application of laser-induced-temperature-jump coulostatics, a new technique for investigating very fast heterogeneous electron transfer. Dynamics associated with electron transfer between redox species (bound or in solution) and an electrode are being probed in the microsecond time domain, will soon be probed in the nanosecond time domain (heretofore virtually inaccessible), and will ultimately be probed in the picosecond time domain. Electronically conducting polymers possess unusual and interesting properties and potential in energy applications, and represent another area of investigation. A significant contribution made here is the development of a theory to explain apparent time-independent hysteresis often observed in the cyclic voltammetry of ion-intercalating systems in general (e.g., electronically conducting polymers and redox polymers). Computer simulation of a variety of electrochemical problems directly related to this project remains a significant and continuing contribution. [2.8 FTE]

12. *Chemical Properties and Reactions of Mono- and Dinuclear Ferrocene Derivatives*
R.B. Klemm

The project objective is preparation of metallocenes and investigation of their properties, particularly as they relate to the oxidation and reduction of water. Preparation of ferrocene derivatives with potentials high enough to oxidize water under neutral or slightly acid conditions are under way. For the reduction of water, mechanisms of the generation of hydrogen from [1.1] ferrocenophanes with strong acids are investigated. Kinetics of hydrogen formation were studied and specific rates for three ferrocenophanes were derived. Results indicate that the orientation of the protons on the iron atoms has a significant effect on the reaction. It is therefore believed that understanding this reaction will enable further modification of the ferrocenophane so that hydrogen might be obtained from weak acids and perhaps even water. Current studies focus on the effect of deuterated acid on the rate of hydrogen evolution and on the composition of the gas to determine the extent of H–D exchange in the ferrocenophane. [0.6 FTE]

Chemistry Department $2,699,000

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

Transient chemical species, such as radicals and ions in unusual oxidation states, are important in many chemical reactions. This project studies the behavior of these transient species, produced by pulse radiolysis or photolysis. Principal areas of investigation are: (1) studies at high pressure of the mobility and reactions of electrons in dielectric fluids; (2) measurements of the Hall mobility of electrons in liquids; (3) studies of the chemistry of iron(IV) and iron(V); (4) hydroxylations and Fenton chemistry; (5) modeling of reactions in heavy-ion tracks; and (6) formation and reactions of transition metal complexes in unusual oxidation states. Studies of transition metal complexes are relevant to reactions for conversion of solar to chemical energy and to the understanding of homogeneous catalysis. Fenton chemistry is of industrial importance. Studies of electrons in fluids are important in understanding the basic processes of radiation chemistry and in developing new detectors for use in high-energy physics. [7.1 FTE]

14. *Thermal and Photoinduced Reactions of Metal Complexes*
N. Sutin, C. Creutz, B.S. Brunschwig,
J. Winkler, E. Fujita

Transition-metal complexes that strongly absorb visible light and readily undergo electron-transfer reactions are excellent mediators of outer-sphere light-induced redox reactions, many of which effect net storage of the light energy. In addition, because of their ability to promote the formation or activation of small molecules, transition-metal complexes can provide homogeneous catalytic routes for the thermal and photochemical formation of H_2 or activation of CO_2. This project encompasses fundamental studies of the reactions of excited- and ground-state complexes in solution. The diversion of a significant fraction of the electronically excited molecules into "useful reactions" must compete with rapid physical deactivation processes (luminescence and radiationless decay) and chemical "back-reactions." Thus, a major objective is the quantitative study and control of these physical and chemical deactivation processes. The lifetimes of excited states and the rates of electron-transfer reactions of excited- and ground-state complexes are being determined and modeled. Because the efficiency of the energy conversion sequence is ultimately limited by the nature and rate of the subsequent chemical steps, mechanistic studies of the reactions of catalytically promising transition-metal ions in high- and low-oxidation states are also being conducted. [9.7 FTE]

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

The rates of chemical reactions depend on electronic degrees of freedom in reacting species. For this reason, collisional transfer or radiative loss of energy is an important part of many reaction mechanisms. In this project, pulsed laser radiation is used to produce translationally energetic (hot) atoms, highly vibrationally excited molecules, or electronically excited atoms. Rates of collisional energy transfer from these energetic species are determined using infrared fluorescence, laser-induced fluorescence, and diode laser absorption spectroscopy. For example, the conversion of electronic energy of $O(^1D)$ atoms to vibrational energy of CO is being studied, using a diode laser probe. In addition, vacuum-ultraviolet radiation from the Dynamic Spectroscopy Beamline of the National Synchrotron Light Source (NSLS) is used to study electronically excited states of molecules and photoionization of ground- and excited-state atomic species. Mechanisms of electronic energy relaxation in gas-, liquid-, and solid-phase cyclohexane have been the subject of recent experiments at the NSLS. Assistance to outside users of this facility is also supported by this project. [5.4 FTE]

16. Hot Atom Chemistry
A.P. Wolf, R.A. Ferrieri

Atom–molecule collisions involving atoms with excess translational and/or electronic energies can, in many instances, initiate unusual chemistry by producing highly excited reaction intermediates. The project objective is to fully understand the mechanisms responsible for energy transfer from excited atoms, particularly through chemical pathways. These studies can aid in understanding the complex chemistry involved in photochemical processes and in high-temperature environments. A new approach being developed generates energetic oxygen atoms through ion beam sputtering. The hot-atom chemistry of oxygen is poorly understood because studies using nucleogenic methods are made difficult by the extremely short half-life of the atom's principal radioactive isotope. The technique is adaptable to gas- and condensed-phase studies, where isolation and detection of structural and stereochemical isomer products provide means to monitor (1) the nature of the chemical interaction and (2) the stability and fate of the reaction intermediate under a variety of conditions. Nucleogenic methods are also used to investigate atom–molecule collisons in the following areas: (1) stereochemical consequences of hot homolytic halogen atom substitution reactions; (2) the effect of kinetic energy on the quenching exit-channels in metastable $^{13}N(^2D,^2P)$ atom collisions with small inorganic molecules; and (3) the reactions of $^{11}C(^3P,^1D)$ atoms with complex organic molecules, and particularly, on the stability of aromatic carbenes. [3.2 FTE]

National Synchrotron Light Source Department **$5,610,000**

17. National Synchrotron Light Source Operations and Development
M.L. Knotek

The project objective is to support operations and development of the National Synchrotron Light Source (NSLS). Operations cover: (1) operation and maintenance of the two NSLS electron storage rings and its associated injector combination of linear accelerator-booster synchrotron; (2) operation and maintenance of the photon beam lines of the vacuum ultraviolet and x-ray storage rings; and (3) the technical support of experimental users. Development of the NSLS includes further improvement of the storage rings by means of new developments in high-resolution photon optics, state-of-the-art monochromators, x-ray mirror systems, and detectors. The NSLS storage rings provide extremely bright photon sources, several orders of magnitude more intense in the vacuum ultraviolet and x-ray regions than conventional sources. An extensive research and development program is necessary to optimize performance characteristics and to develop new beam line instrumentation that will permit users to take advantage of the unique research capabilities offered by this facility. [56.0 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Chemical Biodynamics Division **$996,000**

18. Artificial Photosynthesis
M. Calvin, J.W. Otvos

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

19. Photon Conversion Through Storage of Metastable Molecules

H. Frei

The purpose of this project is to search for and evaluate chemical systems that permit use of near-infrared photons, accomplish their storage, and offer a way for efficient conversion of the stored chemical energy into useful energy. Focus is on two approaches that contribute to this important problem in solar photochemistry. In fundamental studies, we are searching for low energy paths of bimolecular reactions that can be accessed by near-infrared photons. Reactions are induced in cryogenic matrices under selective vibronic excitation. Examples include reactions of singlet O_2 with halogens and of singlet SO with olefins. In experiments directly aiming at photon storage and conversion in room temperature solution, we are studying chemical storage of near-infrared energy carrying O_2 ($^1\Delta$) in the form of aromatic endoperoxides in nonpolar and aqueous solution. Physical deactivation processes and excited-state redox chemistry of O_2 ($^1\Delta$) retrieved from these endoperoxide storage molecules are monitored in real time by laser flash-near infrared chemiluminescence and transient absorption spectroscopy. [1.2 FTE]

20. Chemistry of Electronically Excited Molecules

G.C. Pimentel

This research investigates the chemistry and energy movement as it occurs on electronically excited hypersurfaces. Since both natural and artificial photosynthetic processes depend upon the chemistry of electronically excited molecules, these studies aid in the design of systems for chemical storage of photon energy. Cryogenic solids furnish particularly favorable environments for the study of light-initiated and reaction-initiated movement between and on electronic hypersurfaces. Reactants under study include hydrogen halides with acetylene, mercury, cadmium, and zinc atoms with haloalkanes and haloalkenes; and NH($^1\Delta$ and $X^3\Sigma$) with dimethylacetylene. Fluorescence and phosphorescence intensities are used to reveal transfer from singlet to triplet states. Focus is on energy storage using near-infrared light, photochromism, and hypersurface mapping. Temporal aspects of electronically excited transient intermediates are examined using nanosecond infrared spectroscopy. [6.0 FTE]

Materials and Chemical Sciences Division $434,000

21. Photochemistry of Materials in the Stratosphere

H.S. Johnston

This research is concerned with photochemical molecular dynamics, emphasizing chemical species that occur in the stratosphere. Ultraviolet photolysis of molecules (N_2O_5, NO_2Cl, HNO_3, $ClNO_3$) at low pressure and for short time periods has been found to produce electronically excited nitrogen dioxide, which emits visible radiation. This light is dispersed, represented as a linear combination of monochromatically excited NO_2 fluorescence spectra, and interpreted as an emission probe for the nascent internal-energy distribution of the product molecule. The method of interpreting the data to give molecular internal-energy distributions is novel to our studies. [5.0 FTE]

22. Photon-Assisted Surface Reactions, Materials and Mechanisms

G.A. Somorjai

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

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

$3,000,000

23. Quantum Mechanical Studies of Radiation-Produced Intermediates

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

Electronic structure calculations are being used to theoretically characterize the microscopic properties of matter, emphasizing applications to transient species such as free radicals and energetically excited molecules. These dominate the early processes initiated by radiolysis and photolysis of various media and also occur as important intermediates in many chemical reactions. Because experimental data on such elusive species are often difficult to obtain and interpret, the *ab initio* calculations provide an important source of information on basic quantities such as molecular geometries, potential energy surfaces, spectroscopic parameters, and decay lifetimes. These properties ultimately govern the mechanisms of chemical processes actually observed in studies of radiation chemistry, photochemistry, and reaction kinetics. A new method has recently been developed to characterize the lifetime of an electronically excited metastable system. The procedure, which takes advantage of the mature techniques of bound-state quantum chemistry to provide input for analytic continuation, has been shown to give excellent results for the test case of the lowest Feshbach resonance in H^-. In other work, spin densities have been calculated for the SO_3^- and $PO_3^=$ radical anions and their protonated forms and for the H_2CN, $H(OH)CN$, $CONH_2$, and CH_2CHCH_2 radicals. These have proven useful in interpreting results obtained experimentally by electron spin resonance. [2.7 FTE]

24. Organic Photochemical Processes

P.K. Das

This research encompasses time-resolved studies of physicochemical aspects of organic photoreactions in condensed phases. Primarily based on nanosecond laser flash photolysis and pulse radiolysis, spectral and kinetic information is sought on short-lived photointermediates such as electronically excited states of singlet, doublet, and triplet multiplicities, exciplexes, ion pairs, radicals, biradicals, and zwitterions. Photoreactions of interest are 1,3-cycloaddition, isomerization, rearrangement, oxygenation, ring opening, hydrogen abstraction, and small-molecule extrusion. Model substrates include arylalkanes, cyanoaromatics, carbonyl and thiocarbonyl compounds, three- and five-membered heterocycles, and carbonyl-containing polyenes and polymers. Emphasis is on bimolecular interactions in the form of energy and electron transfer among systems of stable and transient nature. Details of the kinetics and energetics of these processes help us to understand the basic factors that control energy storage, conversion, and dissipation in the course of intermolecular processes initiated by photoexcitation. We are currently studying secondary chemical transformations (e.g., deprotonation, fragmentation, and bond cleavage) that occur in photogenerated radical cations of electron-rich aromatics and heterocycles. The findings are relevant to photochemical reaction mechanisms and to the applicability of radical cations of related systems in storing and relaying photon energy. [6.0 FTE]

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

Basic problems in the photochemistry of coordination complexes are investigated. This project considers: (1) the investigation of magnetic field-induced perturbations on photochemical and photophysical processes, (2) the characterization of sequential biphotonic processes in coordination complexes, and (3) the study of excited-state reactivity in complexes with macrocyclic ligands. Magnetic field-induced perturbations of orbitally degenerated excited states are used as probes of the electronic matrix element in different types of reactions (radiationless relaxation, inner and outer sphere electron transfers, characteristic excited-state reactions). Sequential biphotonic excitations are used to establish new reactivities of electronic states not populated by the absorption of one photon. Focus is on compounds with unreactive lowest lying excited states (phthalocyanines, Cr(III) polypyridine complexes). Photophysical and photochemical studies are conducted with a number of macrocyclic complexes (phthalocyanines and more simple macrocycles), which also involve compounds of metal ions in unusual oxidation states. The compounds selected for this project exhibit direct or sensitized redox reactivity for excitations in the visible region of the solar spectrum and have potential applications in solar photochemistry. [6.8 FTE]

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

Electron spin resonance (ESR) spectroscopy is used to study radical structures, reaction mechanisms, reaction kinetics, and electron spin interactions of radicals produced by *in situ* radiolysis and photolysis. ESR spectra provide definitive information on radical structures and acid–base properties. Time-resolved experiments with pulsed radiation provide information on rates of radical reactions and the electron spin interactions that lead to chemical bonding. Recent measurements on rates of spin trapping provide valuable data for using this technique in chemistry, biochemistry, and radiation biology. Time-resolved microwave dielectric absorption studies are used to determine the degree of charge separation in photochemical intermediates in order to explain changes in reaction mechanisms with solvent polarity. A number of photochemically generated excited complexes (exciplexes) have been found to have smaller dipole moments than previously believed. Experiments are in progress to determine whether these dipole moments vary with solvent. Microwave absorption is also used to measure the yield, properties, and kinetics of charge carriers photoinjected into semiconductor particles and films. This method provides information not otherwise available on systems of importance to solar energy conversion. [9.1 FTE]

27. *Photochemical Processes Following Core Electron Excitation*
R.G. Hayes

The chemical processes that result from excitation of core electrons in molecules are studied in order to clarify the dependence of the chemical processes on the mode of excitation. Core excitation is accomplished by irradiation of the molecules, in the gas phase at low pressure, with photons of an appropriate energy in the range 100 to 500 eV from the National Synchrotron Light Source. The ionic species that result from decay of the core excitation in the molecule are observed by mass spectrometry. The photochemistries of carbon disulfide and of methanol are very sensitive to the mode of excitation, but the large symmetrical molecules studied (benzene and cyclohexane) behave in a similar fashion, regardless of how they are excited. We are refining our observations by studying (1) the kinetic energy associated with the various fragments of a molecule and (2) the correlation between the production of a fragment ion and the ejection of an electron with a certain kinetic energy from the molecule. These experiments allow us to define the pathways of fragmentation with more precision than by merely observing the products of fragmentation. [0.6 FTE]

28. *Photochemical and Photoelectrochemical Processes for Light Energy Conversion*
P.V. Kamat, T.W. Ebbesen

The dynamics and mechanisms of photochemical and photoelectrochemical systems are being investigated to develop and improve energy conversion processes. Time-resolved photoelectrochemical experiments are performed to elucidate the mechanistic features and kinetic details of interfacial processes: photosensitization, phototransformations of adsorbed species, and photocorrosion at single crystal and colloidal semiconductors. Focus is on characterizing trapped charge carriers in semiconductor colloids, such as metal sulfides and selenides using laser flash photolysis and pulse radiolysis. Study of these trapped charged carriers is important because they can greatly influence the photocatalytic activity and surface corrosion of the semiconductor. Study of photochemical systems involves a dual approach. First, using techniques such as pulse radiolysis and laser flash photolysis, individual charge transfer reactions of a given system are characterized, with emphasis on the intermediate radical pair properties. Then, from determining the kinetics and thermodynamics of each reaction, the dynamics of the complete systems are computer simulated to determine the conditions necessary for optimal energy yields. [5.4 FTE]

29. *Statistical Theories of Reacting Systems*
J.J. Kozak

Theoretical procedures are developed to interpret the results of experimental studies on aspects of natural and artificial photosynthesis. An approach based on the formulation and numerical solution of a stochastic master equation is used to study energy transfer and storage in two-dimensional disordered systems. The theory is applied to problems such as (1) concentration self quenching of chlorophyll in lipid monolayers and (2) picosecond fluorescence studies of energy migration in the photosynthetic unit (in the regime where the rates of transfer between donor–donor and donor–acceptor molecules are equal). Using methods based on the theory of finite Markov processes and reaction-diffusion theory, the role of potentials, sequestered reaction domains, local imperfections, cage effects, and the number and distribution of reaction channels are studied to clarify experiments in which organizates may be used in photochemical processes to effect the storage of solar energy. In one application, a mechanism is proposed for the colloidal-catalyst-mediated reduction of water to hydrogen by a reduced electron acceptor. The mechanism has been determined by solving numerically the set of reaction-diffusion equations describing the process, thereby allowing an assessment of the factors that influence the change in concentration, of hydrogen with time, in the presence of a platinum catalyst. [3.0 FTE]

30. Track Effects in Radiation Chemistry
J.A. LaVerne, A. Mozumder, W.J.B. Green, R.H. Schuler

The structure of particle tracks in water and its effect on radiolytic products are being probed using experimental and theoretical methods. Experiments with heavy ions are designed to determine differential radiolytic yields as a function of particle energy, linear energy transfer (LET = -dE/dx), charge, and local energy deposition. These studies are conducted with a variety of ions from 1 to 100 eV/A using the facilities of the Notre Dame Nuclear Structure Laboratory, and with ions of up to 500 eV/A from the ATLAS facility at Argonne National Laboratory. Particle track models are being developed using experimentally available elastic and inelastic cross sections to describe the initial distribution of energy deposition in spurs and the contribution of secondary electrons to heavy-ion tracks. Various kinetic-diffusion models are being employed to follow the subsequent reactions of transient species. Electron–ion recombination is being investigated in liquid argon using cylindrical track models to quantify the yield of free ions. [4.9 FTE]

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

The behavior of excited-state species is investigated in ordered heterogeneous systems to determine the effects of molecular organization on photochemical processes. Focus is on how to utilize molecular organization to control the behavior of unstable intermediates, and hence to control photochemical processes of interest in solar energy storage. While micelles, vesicles, and liquid crystal systems are used, spread monolayers are most widely used because they provide the best means for controlling and simultaneous monitoring of molecular organization. Both steady-state and time-resolved fluorescence spectroscopy are used to follow excited-state processes; fluorescence depolarization is used to monitor orientation and rotation of chromophores embedded in the system. Photoreaction product yields are determined by HPLC techniques. These studies involve (1) processes that occur within the layer, such as lateral diffusion, energy transfer, electron transfer, and concentration quenching; and (2) interactions that occur across phase boundaries. Reactions of species originating in the gas phase or subphase with excited states generated in the lipid phase are investigated because of relevancy to processes in more complex organized systems. [6.6 FTE]

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

The Radiation Chemistry Data Center (RCDC) provides information services on radiation chemistry and photochemistry, compiles and evaluates data, and publishes data reviews. The scientific literature reporting kinetic, spectroscopic, quantum yield, or radiation yield data for irradiated systems is included. Bibliographic and numeric data bases are assembled and used with a data base management system for preparing publications such as bibliographies and data tables, and for on-line searching. The *Biweekly List of Papers on Radiation Chemistry and Photochemistry*, the printed version of the RCDC Bibliographic Data Base, is distributed to subscribers. Numeric data bases are built for property data on metastable chemical species and a chemical registry file is maintained for all compounds, ions, and radicals represented in the data files. Data are compiled and evaluated, in collaboration with scientists from other laboratories, for primary excited-state processes of organic molecules in condensed phases and for processes involving transient radicals in aqueous solution. Projects include compilation and evaluation of (1) rate constants for reactions of inorganic radicals in aqueous solution and (2) quenching rates for excited metal complexes in fluid solutions. A handbook of photochemistry, with extensive tables of photophysical properties, is in preparation. [2.8 FTE]

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

Current radiation chemical studies focus on obtaining detailed information on the reactions of oxygen- and nitrogen-substituted aromatic radicals, which are intermediates in the radiolysis of phenols and anilines. These intermediates are generally important for their major role in many electron-transfer processes. Time-resolved absorption, ESR, and Raman methods are used to study structure and reaction mechanisms. Chromatographic analysis of reaction products provides information on the overall chemistry, with emphasis on the second order combination reactions of radicals produced at high concentrations. These studies provide information on the effect of spin delocalization on product information. Recent developments in ion chromatography are also being used to examine competition between intramolecular processes resulting from electron attachment. Scavenging approaches are being developed to examine the distribution of hydrated electron lifetimes in fast-electron and heavy-ion radiolysis. Resonance Raman studies of the radical anions produced in the radiolytic reduction of aromatic carboxylates are also being conducted. [15.0 FTE]

Solar Energy Research Institute
Golden, Colorado 80401

Solar Fuels Research Division	**$805,000**

34. Model Systems for Artificial Photosynthesis
J.S. Connolly

This project focuses on fundamental aspects of light-induced electron transfer in model systems leading to the design and assembly of a synthetic photoreaction center. The approach involves synthetic, structural, spectroscopic, photophysical, and photochemical studies of electron-transfer reactions from excited states of a variety of organic and organometallic systems. The experimental focus is on the properties of porphyrins and related cyclic tetrapyrroles, with emphasis on systems that mimic the reaction centers of natural photosynthetic organisms. Current investigations are concerned with covalently linked donor–acceptor complexes (e.g., porphyrin–quinone molecules). We have synthesized some new molecular systems to study the effects of distance, extended conjugation, and energetics on the rates of intramolecular electron transfer. We are gradually changing the project emphasis to include studies of the role of the medium in influencing the rates and mechanisms of excited-state quenching processes. The media of interest include organic solvents of varying dielectric strength and aqueous vesicles as a means of exercising electrostatic control to achieve high yields of vectorial electron transfer. We plan future studies of other matrix effects, specifically the role of synthetic and biological polymers in facilitating and stabilizing light-induced charge separation. [0.75 FTE]

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

Basic research is being conducted on modified electrodes in (1) water-oxidation catalysis; (2) chemistry and physics of conductive polymers; and (3) polymer–semiconductor, polymer–metal, and polymer–solution junctions. Solid-state and electrochemical properties of a relatively new conductive polymer, polyselenophene, have been studied in detail by ultraviolet-visible and infrared spectrophotometry, x-ray photoelectron spectroscopy, electron spin resonance spectroscopy, dc conductivity, and scanning electron microscopy. Bipolarons are found to be predominant in the electrical conduction mechanism. Similar analytical techniques are being applied to poly(3-methylthiophene), to yield new insight into the role of charge-compensating ions in the conduction mechanism. Extensive research has been completed on the preparation and characterization of an important, new homogeneous catalyst formed *in situ* from *cis*-$RuL_2(OH_2)_2$, where L = 2,2′-bipyridine-5,5′-dicarboxylic acid. The catalyst is a binuclear complex that shows high activity and durability for water oxidation. [1.46 FTE]

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

Research in photoelectrochemistry is concentrating on one- and three-dimensional quantization effects in superlattice electrodes and in very small colloidal semiconductor particles, respectively. Lattice-matched superlattices (LMS) have been studied for the first time in photoelectrochemical cells and show very nice photocurrent spectra that match the theoretical energy-level structure for the quantum wells. Previous results for strained layer superlattices (SLS) were found to contain interferences from the supporting buffer layers. It is not yet established with certainty whether electron transfer from excited states in the quantum wells of SLS or LMS electrodes occurs in our experiments. A detailed kinetic model for electron transfer from superlattice electrodes has been developed further to more rigorously define conditions required for hot-electron transfer. Research on quantized particles has been extended to layered semiconductors, such as HgI_2. The possibility of transitions to higher quantum states in quantized particles has been considered, and the selections rules for optical transitions in such particles have been derived. The possible existence of "magic numbers" in semiconductor colloids has been shown to be ambiguous. [3.6 FTE]

Chemical Physics

Ames Laboratory
Iowa State University
Ames, Iowa 50011

Fundamental Interactions Program **$650,000**

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

New classical, semiclassical, and quantum mechanical scattering theories for reactive collisions between gas-phase molecules are devised. This work provides powerful methods for investigating reaction dynamics in systems of importance in combustion. These investigations are also incorporated into a statistical mechanical development of the kinetic theory of polyatomic gases in which transport, relaxation, and reactive processes are of interest. The dynamics and statistics of distributions of molecules adsorbed on surfaces under nonequilibrium conditions are analyzed via master equations. Such a theory is important for the appropriate interpretation of surface spectroscopic data. This analysis incorporates the effect of interactions between adsorbed surface species on the selection of binding sites, a study of island formation via direct adsorption and surface migration mechanisms, and adsorbate effects on the catalytic properties of surfaces. Another activity involves developing new, efficient methods for accurately predicting interaction energies in small and large molecular clusters. [1.25 FTE]

38. Atomic, Molecular, and Free Radicals: Crossed Beam Kinetics
C.Y. Ng

This project involves the study of the mechanisms and dynamics of fundamental processes that are relevant to combustion and plasma chemistry. Different experimental approaches combining the merits of the molecular beam method, photoionization and time-of-flight mass spectrometry, and laser spectroscopy are being developed in order to measure reaction cross sections of elementary chemical reactions at well-defined collision energies and internal states of the reactants and to identify the kinetic and internal energy distributions of the products. Research includes (1) neutral–neutral interactions by the crossed molecular beam method, (2) high-resolution photoionization studies of hydrocarbon clusters and high-temperature vapors, (3) state-selected and state-to-state ion–molecule reactions (emphasizing charge exchange and proton transfer reactions), (4) vibrational relaxation of simple molecular ions, and (5) laser photofragmentation spectroscopy of polyatomic molecules. [5.50 FTE]

39. Molecular Bonding Theory
K. Ruedenberg

Properties of molecules such as geometric shapes, the behavior in electrical and magnetic fields, optical spectra, and in particular the energy changes that occur during chemical reactions are determined through quantum mechanical *ab initio* calculations of their electronic structures. Energy hypersurfaces that determine the course, directions, and rates of chemical reactions are mapped out as functions of atomic displacements, and their distinctive features are elucidated. Reaction energies, activation energies, transition states, and elusive intermediates are predicted. The electronic rearrangements that occur along reaction paths and their energetic and kinetic implications are analyzed. Fundamental theoretical and computational advances are made in many-electron quantum mechanics, including electron correlation, to establish practical methods for predicting reaction mechanisms with an accuracy that is useful to experimental chemists. Quantitative formulations of interpretative chemical concepts are developed and implemented by determining rigorous contributions of interatomic interactions to provide a reliable basis for the intuitive anticipation of difficult rigorous calculations. These methods are used to study oxidation–reduction reactions, exchange reactions, and isomerizations involving carbon, nitrogen, oxygen, hydrogen, and fluorine atoms. Of particular interest are reactions occurring in combustion, in the atmosphere, and during hydrogenations. [1.5 FTE]

Argonne National Laboratory
Argonne, Illinois 60439

Chemistry Division **$3,505,000**

40. *Photoionization–Photoelectron Research*
J. Berkowitz

Fundamental processes in the photoionization of atoms and small molecules are studied in the vacuum ultraviolet at high photon resolution. For molecules, alternative decomposition modes are investigated to provide important thermochemical values, and structural and dynamical information. Currently, transient species (free radicals, atoms) are being prepared *in situ* by pyrolysis, electrical discharge, or chemical reaction. The atomic studies provide a basis for systematizing and understanding autoionization behavior. The free-radical studies also enable one to infer accurate thermochemical bond energies. 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 the interaction of ultraviolet laser radiation with selected molecular ions. [3.4 FTE]

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

The project objective is to characterize the dynamics of elementary chemical reactions in the gas phase, emphasizing reactions of importance in the oxidation of hydrogen and simple hydrocarbon fuels. The project combines an ongoing theoretical effort with a new experimental initiative in chemical dynamics and kinetics. The theoretical effort focuses on calculating accurate molecular interaction energies, studying the dynamics of reactions on the computed surfaces, and developing the mathematical/computational methodology needed to accurately model chemical systems. The experimental initiative consists of studies (1) of the kinetics of reactions in shock tubes, emphasizing reactions involving hydrogen atoms; and (2) of the dynamics of reactions, using pulsed molecular beam techniques capable of both angle- and state-resolved measurements. In order to provide detailed information on all of the factors that govern chemical change, we intend to compute/monitor all of the product channels involved in the elementary processes studied. [15.0 FTE]

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

The study of heterogeneous catalysis on a molecular level is pursued. Beams of catalytically active naked metal (nickel, chromium, vanadium, silver, copper, aluminum, iron) atom clusters containing two to several hundred atoms are generated by pulsed lasers, and their physical and chemical properties are characterized by laser-based, in-flight diagnostic techniques. Spectral and electronic properties are determined and experimental results are correlated with theoretical calculations. Mechanisms, energetics, and kinetics of cluster chemical reactions and of adsorption and catalytic processes on cluster surfaces are determined by the flow tube technique. The transient products are identified by laser ionization mass spectrometry. [9.3 FTE]

Brookhaven National Laboratory
Upton, Long Island, New York 11973

Department of Applied Science **$625,000**

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

The objectives of this multitechnique project are (1) to determine absolute rate constants for elementary combustion-related reactions over a wide temperature range and (2) to investigate mechanistic factors involved in gas-phase combustion and pollutant formation processes. Emphasis is on alternative fuels that comprise a range of fuel types, including hydrogen, alcohols, and hydrocarbon synfuels. A facility has been developed that features experimental techniques including: (1) flash photolysis-resonance fluorescence (FP-RF); (2) discharge flow-resonance fluorescence (DF-RF); (3) flash photolysis-shock tube (FP-ST); and (4) discharge flow-photoionization mass spectrometry (DF-PIMS). The FP-RF and DF-RF methods are used to determine specific rate constants for a large number of elementary atom–molecule and radical–molecule reactions over a wide temperature span, ~200 to 1,100 K. The recently developed FP-ST apparatus significantly extends this project's capabilities for direct rate measurements into the combustion temperature regime. With this device, kinetic studies are performed over a temperature range from ~800 to 2,000 K; and thus these measurements overlap the temperature range of the other, more conventional techniques used in this project. The DF-PIMS method is used for direct observations of reactants and products for elementary reactions to investigate the relevant reaction mechanisms. This DF-PIMS experiment utilizes ultraviolet radiation at the National Synchrotron Light Source to achieve specificity and selectivity in obtaining photoionization mass spectra. [6.6 FTE]

Chemistry Department $2,850,000

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

The project objective is to apply theoretical methods (1) to the study of energy flow in chemical reactions and (2) to the elucidation of molecular interactions involved in the storage and interconversion of energy in the gas phase and in condensed phases, including phenomena associated with charged species (i.e., solvation and charge-transfer processes). Methods include (1) *ab initio* and semiempirical calculations of the energies and structures of molecules in specific electronic states and (2) classical and semiclassical treatments of the nuclear motion in kinetic processes involving these systems. Focus is on: (1) *ab initio* models for aqueous charge-transfer processes and related electronic structure properties of transition metal complexes and the role of solvent dynamics in controlling charge-transfer kinetics; (2) dielectric effects of solvents surrounding cavities of various shapes; (3) application of statistics for free-energy correlation methods to chemical and physical properties of large molecules; (4) dynamics and energetics of elementary gas-phase reactions; and (5) dynamics of intramolecular energy transfer and of reactions involving excited states of atoms and molecules. Many of the techniques currently being developed and applied in this project are useful for analyzing and interpreting experimental data obtained at the National Synchrotron Light Source (NSLS), the High Flux Beam Reactor (HFBR), and in other experimental programs in the Department. [5.4 FTE]

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

Hypervelocity, large-cluster impacts on surfaces have demonstrated sputtering ratios and sputtering mechanisms that are significantly different from atomic ion sputtering. The transfer of kinetic energy from projectile to target species generates thermal spikes with relatively small surface-to-volume ratios, and much larger fractions of deposited energy are dissipated in evaporative than in conductive cooling. Investigation of the energy distribution of sputtered atomic or molecular species and the chemical constitution of these species will provide information on the dynamics of energy transfer in larger cluster impacts. These impacts generate large assemblies of atoms under transient extreme conditions of temperature and pressure giving rise to large numbers of energetic gaseous species that have application in subsequent reactions of chemical interest. Cluster impacts can be used to alter surface architecture with a high degree of control, to generate microscopic craters or holes in thin films, and to remove very thin surface layers. [5.4 FTE]

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

The first objective of this project is to understand the potential hypersurface of pairs of reactive molecules at separations larger than those at which reaction occurs. Such information is necessary to make accurate predictions of reaction rates. Photoionization mass spectrometry is being used to measure dissociation energies of van der Waals complexes and clusters of the reactive molecules. Heats of formation are determined for free radicals and molecular fragments, neutral and ionic, that frequently appear as reaction products or energetic reaction intermediates. Mechanistic information is being sought from studies of photoionization-induced dissociative rearrangement processes in weak heterodimers. The second objective is to explore and characterize the photoexcitation and subsequent ionization processes of resonantly excited molecules. A general study of the ionization dynamics of neutral molecular ground and excited states utilizing both synchrotron and laser radiation is under way. Analysis of electron or photon emission following vacuum ultraviolet single-photon ionization and resonant multiple-photon excitation and ionization of small molecules is being conducted. Three measurements provide a detailed probe of the vibronic structure, spatial orientation, and ionization dynamics of neutral excited states lying in or below the ionization continuum. [4.3 FTE]

47. *Molecular Structure and Chemical Reactivity on Surfaces*
J. Hrbek, T.K. Sham

The main objective of this research is to elucidate the nature of the electronic interactions between surfaces and adsorbates, and the manner in which interactions between adsorbed species are mediated by surface atoms, with emphasis on technologically important materials. Identification of the molecular structure of surface intermediates, active sites on surfaces, and the effect of promoters and poisons on surface selectivity and activity will help to provide the fundamental understanding necessary for controlling the chemistry occurring on these surfaces. These studies are being carried out through photoelectron spectroscopy, thermal desorption, electron diffraction, vibrational spectroscopy, and the development and application of synchrotron radiation spectroscopies, e.g., photoelectron and x-ray absorption (XANES and EXAFS). Results of these studies are directly related to kinetic and mechanistic aspects of chemical reactivity and catalysis. [2.1 FTE]

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

Research in this project focuses on structural investigations of materials important to energy systems (e.g., zeolites, clathrates, transition metal hydrides, dielectrics, and fast-ion conductors). The project makes extensive use of facilities at the High Flux Beam Reactor and the National Synchrotron Light Source. For materials where hydrogen and other low-Z atoms are emphasized (e.g., transition metal hydrides) and for disordered systems (e.g., fast-ion conductors), neutron diffraction has special advantages for determining structure and investigating chemical bonding. At the synchrotron, the unique characteristics of the x-ray source are being exploited to define new areas of crystallographic research, for example in experiments with extremely small zeolite single crystals and in time-resolved studies of dielectric materials under an applied electric field. [5.1 FTE]

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

A variety of laser spectroscopic techniques are applied to problems involving the structure and reactivity of short-lived molecular fragments in gas-phase chemical reactions. The behavior of such species often governs the rates and pathways of important reactions in combustion and plasma chemistry. The goals of the project are (1) the elucidation of molecular structure and intra- and intermolecular potential functions and (2) the estimation of reaction intermediate concentrations and reaction rates. [2.5 FTE]

Lawrence Berkeley Laboratory University of California

Berkeley, California 94720

Applied Science Division $142,000

50. *Combustion Chemistry*

N.J. Brown

Combustion chemistry consists of complex chain mechanisms involving radical and stable species. The study of combustion chemistry in realistic combustion systems is impeded by the inherent difficulties encountered in performing measurements in high-temperature environments where the chemistry is frequently coupled to fluid mechanics. The application of various theoretical approaches to the study of thermal and state-to-state reactions is particularly attractive for elementary reactions and processes important in combustion because it offers the long-term possibility of prediction. This approach is further strengthened when coupled with an experimental program to verify the theoretical predictions. Task one is concerned with investigating the dependence of reactivity and energy transfer processes on various types of energy, angular momentum, and potential energy characteristics. Dynamical and statistical theoretical approaches are being pursued using realistic potential energy surfaces for prototypical molecular systems important in combustion systems. Task two is concerned with investigating ignition chemistry. Ignition can be initiated by the photodissociation of sensor molecules, and can be investigated theoretically and experimentally. Laser-induced chemistry, molecular beam mass spectroscopy, and other laser-based spectroscopies will be used to characterize ignition phenomena and to measure important rate coefficients. [1.0 FTE]

Materials and Chemical Sciences Division $2,320,000

51. *Energy Transfer and Structural Studies of Molecules on Surfaces*

C.B. Harris

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

52. *Crossed Molecular Beams*

Y.T. Lee

The major focus of this research project is to elucidate detailed dynamics of simple elementary reactions that are theoretically important and (using the molecular beams method) to unravel the mechanism of complex chemical reactions or photochemical processes that play an important role in many macroscopic processes. Molecular beams of reactants are used to study individual encounters between molecules or to monitor photodissociation events in a collision-free environment. Most of the information is derived from measurement of the product fragment energy and angular distributions, using a unique molecular beam apparatus designed for these purposes. Activities are centered on the following areas: (1) the direct probing of transition states of the $F + H_2$ reaction through the experimental observation of quantum mechanical resonance phenomena; (2) the mechanisms of elementary chemical reactions involving oxygen atoms with unsaturated hydrocarbons; (3) the dynamics of chemical reactions of electrochemically excited atoms; (4) the primary photochemical processes of polyatomic molecules and radicals; (5) intramolecular energy transfer of molecules chemically activated and locally excited using overtone excitation processes; (6) infrared absorption spectroscopy of hydrated hydronium ions; and (7) studying the energetics of polyatomic radicals by photofragmentation and photoionization techniques. [10.5 FTE]

53. *Molecular Interactions*

W.A. Lester, Jr.

This project is directed at extending fundamental knowledge of atoms and molecules, including their electronic structure, mutual interaction, collision dynamics, and interaction with radiation. The approach combines the use of (1) *ab initio* methods, such as multiconfiguration Hartree-Fock, configuration interaction, and the recently developed quantum Monte Carlo (QMC), to describe electronic structure, intermolecular interactions, and other properties; (2) various methods for characterizing inelastic and reactive collision processes; and (3) photodissociation dynamics. Focus is on (1) the development of efficient methods for generating optimum importance functions in QMC, (2) the introduction and application of effective-core-potential methods in QMC, and (3) an adiabatic treatment of single-photon indirect polyatomic photodissociation with emphasis on product rovibrational photofragment distributions. [6.0 FTE]

54. *Theory of Atomic and Molecular Collision Processes*

W.H. Miller

This research is primarily involved with the development of theoretical methods and models for describing atomic and molecular collision processes. Specific topics of interest include the theory of inelastic and reactive scattering, collision processes involving electronically excited atoms or molecules, collisional ionization phenomena, statistical theories of chemical reactions, scattering of atoms and molecules from surfaces, and the interactions of molecular systems with high-power laser radiation. Much of this research is involved with the development and application of a general semiclassical mechanics that allows combination of classical mechanics and quantum mechanics in a correct and useful manner. This has been extremely successful in providing an understanding of the various quantum effects that are seen in molecular phenomena, and it also often provides simpler computational methods for quantitative calculations. Certain research topics are more amenable to a completely quantum mechanical approach, and these sorts of theoretical techniques are also used. The ability to understand, and thus to model and to predict, chemical kinetics phenomena in the gas phase has widespread practical importance in a number of different areas. Among these are atmospheric chemistry and physics, interactions of molecules with strong laser fields, and energy transfer and chemical reactions in flames and combustion. [3.5 FTE]

55. *Selective Photochemistry*
C.B. Moore

The fundamental goal of this project is to understand the photophysics and photochemistry that occur following selective excitation of molecules. Focus is on the chemical reactions of specifically excited states and the dynamics of energy transfer, both within a molecule and to surrounding molecules. For low levels of vibrational excitation in small molecules, individual quantum states may be excited, enabling the measurement of reaction and energy transfer rate constants for each quantum state. For larger or more highly excited molecules, it is usually not possible to excite single eigenstates. Instead, a number of eigenstates are excited simultaneously and a redistribution of the initial vibrational excitation occurs. This process, known as intramolecular vibrational energy redistribution (IVR), is extremely rapid and severely limits the realization of truly mode-specific unimolecular reactions. Studies designed to elucidate the coupling mechanisms and dominant pathways for IVR are currently under way on a number of model systems. The rates and mechanisms of free-radical reactions (e.g., those important in combustion) are often best studied by flash kinetic spectroscopy using lasers for thermal heating, for photolyzing, and for spectroscopic probing. Reactions can be studied as a function of individual quantum states. A fundamental understanding of these reactions is sought to serve as a basis for modeling combustion processes. [4.0 FTE]

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

The project objective is the discovery and development of methods of calculation of thermodynamic and related properties of important chemical systems by use of quantum and statistical mechanics together with experimental measurements for key systems. Primary emphasis will be on ionized systems, electrolyte solutions, and plasmas. Recently the critical points for pure NaCl and KCl were predicted from a combination of rigorous statistical thermodynamics (for the vapor) and an extrapolation of the empirical equations (for the liquids). With guidance from corresponding states theory, a fused salt–polar liquid system was discovered with a critical point at 140°C, where detailed laboratory study is feasible. Measurements of electrical conductance and other properties are proceeding for this system. The effect of ionic forces on the large-scale fluctuations near a critical point is being studied theoretically and experimentally. Earlier advances yielded improved equations for electrolyte solutions, which are now being applied to a wide variety of systems of industrial or geological interest (including geothermal brines). Recent efforts also included relativistic quantum mechanical methods for calculating energies, bond distances, and other properties of the ground and excited states of molecules containing very heavy atoms, where the conventional nonrelativistic methods are inadequate. Such results are important in evaluating possible laser systems and for models of catalytic entities including heavy atoms (e.g., platinum). [2.2 FTE]

57. *Far-Infrared Laser Spectroscopy of Reaction Intermediates*
R.J. Saykally

Sophisticated far-infrared laser techniques are combined with laser photolysis and supersonic beam technology for the study of spectra, structures, potential surfaces, and dynamics of molecules that are intermediates in chemical reactions. Anisotropic bimolecular potential energy surfaces are obtained from the direct measurement of vibration-rotation spectra of van der Waals bonds in molecular complexes. Both nonreactive (e.g., Ar–HCl) and reactive (e.g., F–HF) bimolecular systems are studied. This work complements the measurement of bimolecular potential surfaces by molecular beam scattering experiments. The structures and dynamics of molecular complexes are also studied as a route to understanding the dynamical properties of condensed phases. [4.8 FTE]

58. *Potential Energy Surfaces for Chemical Reactions*
H.F. Schaefer, III

This research project has two goals, related yet distinct. The first goal is the development of new theoretical and/or computational methods for describing what electrons do in molecules. The single outstanding problem in the field is the correlation problem, that of formulating models for going beyond the single-particle or Hartree-Fock approximation. The second goal is to apply these theoretical methods to significant problems of broad chemical interest, through: (1) model theoretical studies of chemisorption, metal clusters, and organometallic species; and (2) studies of potential energy surfaces that govern gas-phase chemical reactions. Research in the former area is ultimately aimed at a true molecular understanding of catalysis, a subject pertinent to future energy requirements, which is sometimes approached by trial and error methods. In the latter area, research sometimes tends toward molecules potentially important in combustion or atmospheric chemistry and the development of high-power laser systems. Theoretical chemistry has become a significant source not only of broad generalities, but also of specific predictions concerning molecular systems that may be very important, but inaccessible to experiment. [5.5 FTE]

59. *Photoelectron Spectroscopy*
D.A. Shirley

The major project objective is to conduct exploratory research on the interaction of vacuum ultraviolet and soft x-ray radiation with matter, emphasizing synchrotron radiation and photoelectron spectroscopy. The project also supports the national programs through innovation and development of new experimental methods based on synchrotron radiation in the energy range 10 to 4,000 eV, and through the training of doctoral candidates in the use of synchrotron radiation. The reaction of radiation in this energy range with matter yields (as one reaction product) an unbound electron in a highly excited final state. The further interaction of this electron with the other reaction product(s) can provide unique and definitive information about both reactants and products. Focus is on (1) understanding of electron correlation in atoms and small molecules, including the characterization of continuum resonances and correlation satellites, and (2) characterization of the atomic and electronic structure of surfaces. This includes both structural studies by photoelectron diffraction (ARPEFS) and electronic structure determinations on and near the surface. Related supportive research includes photoelectron spectroscopy in molecular beams and high-resolution electron energy loss spectroscopy on surfaces. [10.0 FTE]

Lawrence Livermore National Laboratory
Livermore, California 94550

Division of Chemical Engineering $40,000

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

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

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Chemistry Division $370,000

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

The project studies the photoelectron dynamics of molecules and metal vapors, using angle-resolved photoelectron spectroscopy and synchrotron radiation. Phenomena investigated include: (1) autoionization, (2) shape resonances, (3) the Cooper minimum, (4) correlation satellites, (5) interchannel coupling, (6) multiplet structure, and (7) preionization resonances. Systematic studies are pursued on iodine-containing molecules, triatomic molecules, surface-oriented molecules, and various metal vapors, including zinc, cadmium, mercury, manganese, and gallium. Supportive calculations using the multiple-scattering Xα method are performed and correlated with observed cross sections and angular distribtion parameters. Improved computer handling of the experiment allows the introduction of constant-ionic-state techniques. Besides providing fundamental information in atomic and molecular science, the project supplies data and ideas for studying molecules adsorbed on surfaces, clarification for solid-state properties in metals, and an understanding of clusters. [2.1 FTE]

Sandia National Laboratories
Livermore, California 94550

Combustion Research Facility $5,435,000

62. *Flame Dynamics Research*
R. Cattolica, W. Flower

The purpose of this research is to investigate the interactions between chemical species, temperature, and fluid motion as they relate to the formation of soot in flames. Soot size and number density, and the effect of elevated pressure on these quantities, have been determined in laminar diffusion flames, using static and dynamic light scattering. Local soot-formation rates have been determined using laser-velocimetry flow-field measurements and light-scattering measurements of soot concentration. Laminar axisymmetric ethylene-air diffusion flames have been studied at pressures up to 10.0 atm in order to examine how the balance between soot formation and oxidation processes changes with pressure. The extent of soot removal by oxidation is observed to decrease rapidly as pressure increases. Measurements of the emission and absorption of near-infrared radiation by soot particles have been used to determine the soot particle temperature as a function of axial position in order to examine the effect of radiant thermal losses on soot formation and oxidation processes. A counter-flow diffusion flame has been used to study the impact on soot formation of effects due to dilution of the fuel, preferential diffusion, and oxygen addition to the fuel. Results obtained when inert diluents of varying molecular weight were added to the fuel show a strong correlation between the mobility of the inert and the amount of soot that is formed. These results show that concentration modification due to preferential diffusion can play a significant role in the soot-formation process. [2.0 FTE]

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

This research is directed toward an increased understanding of the coupling between the chemical kinetic and turbulent transport processes occurring in chemically reacting flows. The long-term goal is to use these data to improve predictive capabilities in turbulent combustion. A parabolic flow jet flame and an elliptic flow, bluff-body flame are investigated. Multispecies Raman concentration and temperature measurements, combined with simultaneous velocity determinations, have been compared with model predictions to estimate the influence of chemical nonequilibrium on mean turbulent flame quantities. One- and two-dimensional imaging of major and minor species is producing new insight into mechanisms of local flamelet burning and extinction. A chemically reacting turbulent flow cooperative group comprised of participants from private industry, universities, and Sandia National Laboratories has been formed and meets on a biannual basis. [3.0 FTE]

64. *Combustion Research Facility (CRF) Operations and Visiting Scientist Support*

G.B. Drummond

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

65. *Combustion Research Facility (CRF) Diagnostics Research: Coherent Raman Processes*

R.L. Farrow, L.A. Rahn, R.P. Lucht, R.E. Palmer

This project aims at developing coherent Raman diagnostic techniques in support of CRF programs. Detailed studies are made of the significance of several factors for experiments using CARS, a leading technique for time-resolved measurements of temperature and major species concentrations. These factors include laser photon statistics, Stark effects, laser lineshape convolutions, *in situ* normalization, and interferences between resonant Raman and nonresonant background contributions. A new, high-resolution CARS system is used to examine saturation (another consideration when analyzing CARS measurements) and to determine nonresonant backgrounds of fuel molecules. The modification of CARS spectra at high pressure due to collisional narrowing is quantified in detail using high-resolution CARS and high-resolution inverse Raman spectroscopy, so that measurements in high-pressure environments (e.g., internal combustion engines) can provide more accurate results. Inverse Raman spectroscopy is also used to develop a high-resolution data base of spectral parameters for important combustion species such as nitrogen, carbon monoxide, hydrogen, and water vapor. [5.0 FTE]

66. *Flame Chemistry: Modeling and Experiments*

G.A. Fisk, J.A. Miller, R.J. Kee, L.R. Thorne, D.W. Chandler

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

67. *Chemical Kinetics and Dynamics*

G.A. Fisk, F.P. Tully, R.A. Perry, D.W. Chandler, C. Melius, J.A. Miller

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

68. *Combustion Research Facility (CRF) Diagnostics Research: Advanced Methods*

J.E. Goldsmith, M.L. Koszykowski, A. Lau, F.B. Trebino, R.E. Palmer

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

69. *Combustion Research Facility (CRF) Central Laser Systems*

R.L. Schmitt, R.L. Farrow, L.A. Rahn, R.E. Palmer

This project includes the continued development of existing CRF central lasers and research in support of future major laser systems. The tunable dye laser (DIANA) is used by Sandia staff and visiting scientists for single-shot temperature, density, and species concentration measurements, and for two-dimensional imaging of turbulent nonpremixed flames. A multipurpose laser system (Sirius) consists of a frequency-doubled Nd:YAG laser and several dye laser options, including a broad-band dye laser and a pulse-amplified ring dye laser. When the Nd:YAG laser is operated in single-axial mode in combination with the ring dye laser, the spectral resolution for CARS and other nonlinear spectroscopy experiments (performed in any of the CRF laboratories via the beam distribution system) is as small as a few thousandths of a wave number. Sirius is used frequently for CARS measurements in flames with large luminous backgrounds (e.g., heavily sooting flames or flames laden with coal particles). A third central laser (Dyeblaster) consists of a frequency-doubled Nd:YAG laser and is used routinely to pump dye lasers in user laboratories throughout the CRF. Present laser research in support of advanced central lasers includes diode-laser injection locking of Nd:YAG lasers for stable single-axial-mode operation, and studies of advanced dye laser design. [3.0 FTE]

Atomic Physics

Argonne National Laboratory
Argonne, Illinois 60439

Physics Division **$1,583,000**

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

Resonant laser excitation is used to study molecular and atomic ion structures. High spectral resolution is achieved by collinear excitation of fast ion beams with CW narrow-frequency laser beams. Work on molecular ions is aimed at achieving understanding of both electronic and geometrical structures of simple systems. We are testing *ab initio* theoretical understanding of hyperfine structure in rare-earth ions, plus the fundamental problems of relativistic quantum mechanics and QED in few-electron systems. Some collision studies of fast ions in solids and gases are continuing. [5.1 FTE]

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

This project is directed toward increasing our understanding of atomic and molecular structure through high-resolution laser and radiofrequency studies of many-electron atoms, small molecules, and slow ions, with emphasis on ensuring that the studies are both systematic and of high precision. Significant results were achieved in all three areas during the past year. Comparison of our new hyperfine structure (hfs) studies in LaI_3 with new *ab initio* calculations reveals unexpected shortcomings in the multiconfiguration Dirac-Fock (MCDF) theory. Efforts are now under way to attempt to understand the problem. Studies of the spin–rotation interaction in the diatomic radical YO reveal strong and completely unexpected perturbations that can only arise from a very low-lying electronic state not predicted by the *ab initio* theory. The YO studies are part of a systematic comparison of the related molecules LaO (reported last year), YO, and ScO (currently under study). Our first observations of laser-rf double resonance in atomic ions (with collinear laser and ion beams) were achieved this year in $^{151,153}Eu^+$ using a new low-energy ion apparatus. The linewidths achieved are by far the narrowest yet seen with ion beams, and the technique will allow a systematic comparison of the hfs of ions with that of related neutral atoms at high precision. [1.4 FTE]

72. *Atomic Physics at ATLAS*
R.W. Dunford, H.G. Berry, E.P. Kanter

Research involves both atomic collisions and structure, using a wide range of ion species and energies. Using beams produced by ATLAS, spectra of highly charged ions are used to measure 1s and 2s Lamb shifts in highly charged hydrogen-like atoms. Precision measurements of two- and three-electron ions are made to probe the high-field regime of quantum electrodynamics. Measurements were made in the two- and three-electron ions of titanium and nickel. Plans are under way for measurements of vacuum ultraviolet spectra of highly ionized bromine and for x-ray measurements in several hydrogenic ions. [2.5 FTE]

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

Argonne National Laboratory's 4.5-MV Dynamitron accelerator is used to study the interactions of fast (MeV) atomic and molecular ions with matter. A unique feature is the exceptionally high resolution (~0.005° and ~600 psec) in angle and time of flight obtained in detecting particles emerging from the target. A new multiparticle-imaging detector system has been developed to allow detection of multiparticle events consisting of up to eight particles. The main objective is a general study of the interactions of fast charged particles with matter, emphasizing those aspects that take advantage of the unique features inherent in employing molecular-ion beams (e.g., each molecular ion incident upon a solid target forms a tight cluster of atomic ions that remain correlated in space and time as they penetrate the target). In particular, these techniques allow direct determination of the geometrical structures of molecular ions entering the target. These experiments provide a novel method for the direct measure of the nuclear densities within small molecules. [5.1 FTE]

Brookhaven National Laboratory
Upton, Long Island, New York 11973

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

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

Studies of the physics of multiply charged heavy ions are made with synchrotron radiation from the Brookhaven National Synchrotron Light Source (NSLS) and heavy-ion beams from the Brookhaven Tandem Accel-Decel Laboratory (TADL). A dedicated atomic physics station on the X-26C beamline at the NSLS x-ray ring is used for experiments with white or monochromatic x rays. An extended study of the K-shell photoionization of argon produced by filtered white radiation is in progress. Measurements of the charge states and fluorescent radiation and the development of methods for trapping the ions in Penning- and Kingdon-type ion traps are the initial items of interest. The trapped argon ions are used as targets for sequential photoionization to produce mean charge states greater than those found for a single ionization event. The ions can also be extracted from the trap for subsequent use in ion–atom collision experiments. Equipment for crossed photon-ion beam experiments is being developed using a standard ion source. Inner-shell vacancy processes, charge transfer, and equilibrium charge states in ion–gas collisions are studied with negative ions and with positive ions produced by the tandem accel-decel method. [2.6 FTE]

Lawrence Berkeley Laboratory University of California Berkeley, California 94720

Materials and Chemical Sciences Division $294,000

75. *High-Energy Atomic Physics*

H.A. Gould

The goal of this project is to understand atomic collisions of relativistic ions and to test quantum electrodynamics (QED) in atoms of very high atomic number (Z). These are new areas of research that involve physics not accessible at lower energies or with lower-Z ions. Recent results include detailed measurements of cross sections for electron capture in the K shell and higher shells of relativistic xenon ($Z=54$) and ionization of K-shell electrons of relativistic xenon. These and earlier measurements in this project have led to an understanding of relativistic heavy-ion–atom collisions that, in many cases, is now more complete than for nonrelativistic collisions. Present activities include: (1) measurement of ionization of L- and M-shell electrons of relativistic uranium, (2) multiple electron capture and ionization, and (3) (as a test of the higher order terms in the QED self energy) a measurement of the 1s2p $^3P_0$ lifetime in helium-like uranium ($Z=92$). Future experiments will explore a new mechanism for electron capture: capture from electron–positron pairs produced by relativistic ion–atom collisions. Other experiments will examine relativistic heavy-ion–electron collisions, and channeling and polarization of relativistic heavy ions. [2.5 FTE]

76. *Atomic Physics*

M.H. Prior

This project measures atomic parameters that test fundamental theories and advanced calculations in atomic structure, collision processes, and radiative interactions. Selected research topics have relevance to applied areas, such as plasma diagnostics and advanced laser concepts. Current efforts use the intense multiply charged ion beams from the Lawrence Berkeley Laboratory Electron Cyclotron Resonance (ECR) ion source to perform spectroscopic and collision studies. In the area of collision physics, a new low-energy ion beam facility has been constructed to provide ECR-generated ion beams for electron excitation studies relevant to radiative processes in nonequilibrium plasmas. The new facility is also being used to study quasi-molecular x-ray emission effects and angular scattering following charge capture collisions; long-range plans include study of novel surface interactions and collision processes involving excited atoms. Forbidden emission line spectra from metastable, highly charged ions are also studied and provide new values for wavelengths used in plasma diagnostics and determination of atomic structure parameters. [2.7 FTE]

Oak Ridge National Laboratory Oak Ridge, Tennessee 37831

Physics Division $1,318,000

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

R.L. Becker, C. Bottcher

Theoretical predictions, interpretations of experimental results, and detailed calculations are made for atomic collision, radiation, and structure phenomena. Emphasis is placed on reactions of highly stripped ions with atoms, particularly those reactions of importance in fusion energy devices and those studied in atomic high-energy accelerator physics laboratories. Atomic excitation, ionization, and electron transfer (capture) are treated. Recent activities include calculations of subshell vacancy production including the effects of vacancy rearrangement processes, multiple vacancy production in coincidence with the final projectile charge (to separate capture from noncapture events), coincident excitation and ionization, electron ejection and positron production in collisions of very heavy ions with very heavy atoms, and possible magnetic resonances in the scattering of e^+ from e^-. New theoretical approaches include the one-and-a-half center version of coupled-channels theory, the unification of shakeoff theory with collision theory, and the use of basis spline and collocation methods in the numerical integration of time-dependent quantal equations. Computer programs for solution of the time-dependent many-electron Hartree-Fock and one-electron Dirac equations have been developed. [1.0 FTE]

78. *Accelerator Atomic Physics*

S. Datz, P.F. Dittner, P.D. Miller

The project objective is to achieve a detailed understanding of the interactions of high-energy, multiply charged ions with gas and solid targets, with electrons, and with photons, both with and without external applied fields. The primary facility used is the EN-tandem accelerator, and in recent years some experiments have also involved the Holifield Heavy Ion Research Facility (HHIRF). Electron capture, ionization, and transfer ionization have been studied for 0.1 to 1.0 MeV/nucleon highly charged ions colliding with helium. These experiments have been conducted using both the EN Tandem and the HHIRF. Single and double charge transfer cross sections have been measured. Zero-degree electron spectroscopy has been studied in coincidence with transfer ionization (TI), and vacuum ultraviolet photons have been measured in coincidence with capture and with TI. These measurements indicate charge transfer to lower n states with TI than with single capture, in qualitative accord with theory based on level transfer. Dielectronic recombination has been measured for all beryllium-like ions from C^{2+} through F^{5+}, and for all boron-like ions from N^{2+} through F^{4+}. Correlated inelasticity and impact parameter dependence for 10 MeV carbon ions incident on neon and argon have been measured as a function of recoil ion charge state for various combinations of ingoing and outgoing charge state of the carbon ions. Energy resolution of 1.2 keV and simultaneous angular resolution of 0.005° were achieved using the Elbek magnetic spectrograph. A major effort was devoted to the completion of a conceptual design report for a heavy-ion storage ring for atomic physics (HISTRAP). [5.2 FTE]

79. EN Tandem Operations

P.D. Miller, P.L. Pepmiller

The EN-tandem Van de Graaff is operated for atomic physics research. Terminal voltages up to 6.0 MV are routinely achieved, and ions of all elements with $Z < 9$, as well as many heavier ions are available to users. The user group includes members of the physics division, other divisions at Oak Ridge National Laboratory, faculty and students from various universities, and representatives from industry. A VAX-750/CAMAC-based data acquisition system is available to users. Recent major beam usage has included inelasticity and impact parameter dependence studies of charge-correlated multiple ionization of neon and argon by carbon ions, two-electron-correlated transfer studies, dielectronic recombination rate measurements for beryllium- and boron-like ions, convoy electron studies, and zero-degree Auger electron spectroscopy of highly charged ions. [2.1 FTE]

80. Collisions of Low-Energy Multiply Charged Ions

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

This experimental project is aimed at improving our understanding of inelastic collisions of multiply charged ions with atoms and molecules at the lowest attainable interaction energies. The Oak Ridge National Laboratory ECR ion source provides low-energy multiply charged ion beams for these experiments. An ion–atom merged-beams apparatus has been developed and is being used to measure absolute total cross sections for electron capture by multiply charged ions from hydrogen atoms at relative energies ranging from 1 keV/amu to 1 eV/amu. Recent experiments have shown evidence for an orbiting mechanism predicted to give increasing cross sections with decreasing energy at the lowest energies. Experiments are also being performed to measure the energy distribution of electrons ejected in low-energy multiply charged ion–atom collisions, and in glancing collisions of slow, highly charged ions with a solid surface. The energies of these ejected electrons provide detailed information about the states formed in the collision, and about mechanisms for inelastic processes. Recent high-resolution experiments have provided evidence for the important role of correlation effects in double-electron capture by multiply charged ions from helium. [1.2 FTE]

Sandia National Laboratories

Albuquerque, New Mexico 87185

Laser and Physical Chemistry Department-1124 **$153,000**

81. Atomic Processes

A. Owyoung, A.V. Smith

The goal of this project is to develop techniques for more efficient production of vacuum ultraviolet light by means of nonlinear optical frequency mixing. Present investigations focus on using two-photon resonant sum frequency mixing in atomic mercury vapor, particularly for generation of coherent light in the 130-nm region. For this purpose a number of spectroscopic parameters in mercury, of importance for frequency mixing, are measured. These measurements include molecular absorption as well as a large number of f values for which we have devised new and more accurate nonlinear optical methods of measurement. This information makes it possible to calculate and optimize conversion efficiencies in a systematic fashion for the first time. By numerical modeling of the mixing process, we show that mixing efficiencies exceeding 10% should be possible over some wavelength ranges including 130 nm. This is orders of magnitude greater efficiency than previously demonstrated at such short wavelengths. We attempt to make the model calculations as realistic as possible by taking into account all processes that can affect mixing efficiency (e.g., Stark shifts, amplified spontaneous emission, refractive index changes, and photoionization). [1.0 FTE]

Chemical Energy

Ames Laboratory
Iowa State University

Ames, Iowa 50011

Processes and Techniques Program **$995,000**

82. Organometallic Complexes in Homogeneous Catalysis

R.J. Angelici

Although sulfur is removed commercially from thiophenes in crude petroleum by hydrodesulfurization (HDS) over sulfided metal catalysts, the mechanistic details of this process are not understood. The purpose of this project is to develop some understanding of the reactivity of thiophene coordinated to transition metals as might occur on the catalyst surface. It has been found that the π-complexed thiophene in $(\eta\text{-C}_4\text{H}_4\text{S})\text{Mn(CO)}_3^+$ and $(\eta\text{-C}_4\text{H}_4\text{S})\text{Ru}(\eta\text{-C}_5\text{H}_5)^+$ is highly activated to react with model surface species such as hydrides and sulfides. Reaction with acids leads to the formation of 2,3-dihydrothiophene, a possible intermediate in the HDS process. Reactivity studies of 2,3-dihydrothiophene to determine how sulfur is removed from this molecule are also in progress. These studies are revealing the properties of catalysts that cause them to be active in the HDS process. [3.0 FTE]

83. Chemical Kinetics and Reactivity of Transition Metal Complexes

J.H. Espenson

The primary objective is to provide fundamental data on chemical reactivity bearing on chemical reactions involved in homogeneous catalysis, synthetic fuels, the Fischer-Tropsch process, and the control of acid rain. The principal approach is based on the study of chemical kinetics and reaction mechanisms using a wide variety of experimental techniques applied to reactions occurring from microseconds to days or longer. The reactions under investigation include spontaneous and induced decomposition, heterolytic and homolytic metal–carbon bond cleavage (and the associated bond-dissociation energies), radical-induced electron transfer, free-radical displacement, alkyl transfer, and insertion into metal–metal and metal–carbon bonds. The chemical entities under study include organometallic derivatives of cobalt, chromium, nickel, and rhodium; dinuclear complexes of platinum, nitrogen oxides, and oxoacids; sulfur dioxide; and molecular elements (e.g., S_8 and P_4). [4.4 FTE]

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

Nuclear spin dynamics are used to probe the physics and chemistry of materials involved in heterogeneous catalysis, coals and coal products, and materials science. Examples include precursor pitches used in electrodes for aluminum production, zeolitic catalysts used in conversion of methanol to ethylene, bimetallic catalysts, heavy-metal halide cluster compounds, and amorphous semiconductors used in photoconversion. [3.3 FTE]

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

The goals of this project are to elucidate the chemical and structural properties of highly dispersed supported transition metal catalysts, and to correlate these properties with catalytic performance. Focus is on bimetallic catalysts, catalysts composed of two different metals intimately mixed on the surface of a catalyst support. The catalytic phenomena occurring on bimetallic catalysts may be affected by the abundance and morphology of the surface metal atoms, the relative composition of the constituent transition metals, the nature of the support, the presence of promoters and poisons, and reactant molecules or fragments of molecules that are adsorbed on the surface. The approach is to combine high-resolution solid-state transient NMR techniques with more traditional experimental techniques to examine the nature of supported bimetallic catalysts. This project investigates supported catalysts by (1) determining the state of the metal atoms under reaction conditions, (2) determining the nature of adsorbed species, (3) investigating the chemisorption behavior of simple molecules, and (4) characterizing the catalytic activity and selectivity of model reactions as a function of the state of the catalysts and adsorbed species. [1.4 FTE]

86. 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 used to produce synthetic fuels or to hydrotreat coal-derived liquids are being investigated. Catalysts for energy-efficient routes to specific chemicals are also included. Laser Raman, Fourier transform infrared, and solid-state NMR spectroscopy are being developed for use in the characterization of catalysts and adsorbed species. *In situ* experiments are conducted involving functioning catalysts; simultaneous spectroscopic and kinetic measurements can be performed at the temperatures and pressures typical of industrial operating conditions. These techniques provide a direct method for relating catalyst structure and composition to activity and selectivity. [3.0 FTE]

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

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

Argonne National Laboratory
Argonne, Illinois 60439

Chemical Technology Division **$557,000**

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

This research is designed to determine reaction mechanisms and to explore new catalytic chemistry for converting small molecules (e.g., CO, CO_2, O_2) to desired products. Currently under investigation are main-group soluble oxide catalysts that promote carbon monoxide hydrogenation and water–gas shifting via catalytic chemistry that is distinct from that of other homogeneous catalysts and seems most relevant to suspected metal oxide surface reactions. Also investigated are mechanisms and theory associated with electron transfer processes that occur in the catalytic aerobic oxidations of organic bases, and synthetic methods designed to incorporate shaped regions into phthalocyanine catalysts for homogeneous reactions that occur at high temperatures and pressures. Alternative techniques for adapting multinuclear NMR spectroscopy to high-pressure kinetic studies are also explored. The new chemistry is investigated using a combination of kinetic and spectroscopic techniques in addition to theoretical (molecular orbital) methods. [6.8 FTE]

Chemistry Division **$2,090,000**

89. Inorganic Fluorine Chemistry
E.H. Appelman

This project is directed toward (1) the synthesis and characterization of novel and aggressive oxidants and fluorinating agents, (2) the elucidation of the mechanisms of their chemical reactions, and (3) the development of applications of such compounds as synthetic and analytical reagents. It is also concerned with the use of the techniques of inorganic fluorine chemistry to prepare new compounds of the actinide elements in their highest oxidation states. Current and projected research efforts include a study of the mechanism of production OF_2 in the reaction of fluorine with aqueous solutions, an attempt to synthesize a simple oxide fluoride of neptunium(VII), studies of the infrared spectrum and crystal structure of hypofluorous acid (HOF), and an investigation of the reactions of powerful electrophilic fluorinating agents with organic compounds. [1.6 FTE]

90. *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 eight different premium coal samples. The eight different premium coal samples produced and distributed by this program are (individually) as chemically and physically identical as possible, will have well-characterized chemical and physical properties, and are stable over long periods of time. The coals were mined, transported, processed into desired particle and sample sizes, and packaged in an enclosure that was as free of oxygen as possible and that maintained as much of the natural moisture content as practical to ensure that the coals are kept in as pristine and stable a condition as possible. These premium samples are being distributed to researchers upon request. A computer data base will be included in this program to provide researchers with easy access to detailed information on sample availability, the physical and chemical properties of the coals, and references to the results of research obtained using these samples. [2.6 FTE]

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

This project seeks to reduce the heterogeneity of coals by developing new methods for separating and characterizing coal macerals. The density gradient centrifugation technique developed in this study has provided pure maceral samples for fundamental coal research and samples for the study of coal maceral characteristics, which could lead to improved separation methods. The project focuses on (1) investigating surface properties of macerals with radiolabeling, proton NMR, FTIR, and microcalorimetry to provide information that will be used in improved separation methods; and (2) developing larger scale flow systems using both centrifugation and magnetohydrostatic separations. [3.0 FTE]

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

The major objective of this project is to elucidate the chemical and physical structures of coal macerals and the Argonne Premium Coal Samples. This information will be correlated with the chemical, thermal, and biological reactivity of these substances. Our approach combines selective chemical modification and degradation, and uses a number of instrumental techniques. The study of coal model compounds and realistic model coals synthesized from presumed coal precursors is yielding valuable insights into coal formation and structure. Techniques, such as multinuclear solid NMR, pyrolysis, and fast-atom-bombardment, high-resolution mass spectrometry, are being used to study the macromolecules in coals and coal macerals. The physical structure of coal is being investigated by small-angle neutron scattering and NMR. Information obtained in this study should ultimately help develop more efficient and cleaner ways to use coal. [7.9 FTE]

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

With the availability of samples from the Argonne Premium Coal Sample Program, it is important both to document and understand the chemical and physical changes that may occur in these coals during storage. The project objectives are to examine a select group of properties for the samples and to record any changes with time. Techniques proven to be useful in other areas of fundamental research are being applied to coals in a systematic way for the first time. In addition, this study provides fundamental structural information on this unique set of samples. [2.3 FTE]

Brookhaven National Laboratory
Upton, Long Island, New York 11973

Department of Applied Science **$710,000**

94. *High-Temperature Chemistry*
J.J. Egan

In this project the thermodynamic and transport properties of inorganic substances are investigated at high temperatures using novel techniques to elucidate appropriate atomic models. Substances under study 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 have proven particularly 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. Additionally, solid compound semiconductors of potential use as solar cells are studied by high-temperature coulometric titration methods. [3.7 FTE]

95. *Metal Hydrides*
J.J. Reilly

This project focuses on determining the thermodynamic properties, reaction kinetics, and crystal structure of metal–hydrogen compounds. Specific goals are (1) to relate hydriding properties of metal alloys to their structure and composition, (2) to determine alloy–hydrogen phase diagrams, (3) to determine and systematize crystal structures, and (4) to relate all pertinent data and observations to predict the behavior of a given alloy–hydrogen system. Current topics under active investigation are the development of crystal structure refinement methods for highly strained compounds, improved diffraction techniques employing synchrotron radiation, kinetics of hydrogen absorption by hydride-forming metals, and determination of the relative catalytic activity of the surfaces of such metals. Major experimental tools and/or techniques are x-ray and neutron diffraction, equilibrium pressure-composition measurements, and magnetic susceptibility measurements. [3.9 FTE]

Chemistry Department **$490,000**

96. *Organometallics in Homogeneous Catalysis*
R.M. Bullock, M.A. Andrews

The project objectives are to discover and to understand homogeneous transition metal catalysts that effect important transformations of organic substrates. The new strategies and mechanistic insights obtained will provide guidelines for developing more energy-efficient chemical processes and producing chemicals and fuels from syn-gas and biomass. Current focus is on (1) reactions and properties of metal hydrides, (2) metal-catalyzed epoxidation, and (3) metal-catalyzed reactions of sugars. The first two of these relate to major industrial processes utilizing alkene feedstocks. The hydroformylation, hydrogenation, and hydrocyanation of alkenes are known to involve soluble transition metal hydride complexes as key intermediates. Work in this area focuses on understanding the factors responsible for the different reactivity patterns of these metal hydrides, such as protic (H^+), hydridic (H^-), and radical ($H\cdot$). In the alkene epoxidation studies, the goal is to design and test fundamentally new approaches to more selective and efficient oxidation catalysts. The third area represents a new initiative to explore the possible application of homogeneous transition metal catalysts to biomass conversion. This approach has received little attention to date, but offers potential advantages over traditional, fermentation-based biomass conversion schemes. [3.8 FTE]

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

S. Seltzer

The long-term goal of this research is to elucidate the mechanism of action of the light-driven purple membrane proton pump. The purple membrane captures solar energy and converts it to chemical energy. Absorption of visible light by bacteriorhodopsin and its bound retinal, the membrane's photoactive agents, results in the translocation of protons across the membrane. Light absorption initiates a photocycle during which bacteriorhodopsin's retinal undergoes reversible *cis-trans* isomerizations and leads to changes in its chemical environment, which appear to be necessary for proton pumping and preparation of the membrane for subsequent turnovers of the cycle. How these chemical changes occur and how they drive the pumping process are being investigated. Models for the retinal binding and *cis-trans* isomerization site are being synthesized, combined with retinal, and tested in order to examine proposed mechanisms of *cis-trans* isomerization in bacteriorhodopsin. [1.4 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Materials and Chemical Sciences Division $949,000

98. *High-Energy Oxidizers and Delocalized-Electron Solids*

N. Bartlett

The main aim of this project is the synthesis and characterization of new materials that may have value in electrochemical applications or in the efficient conversion of light to electrical energy. The synthetic work tests models and theories that correlate physical properties (such as electrical conductivity) with chemical composition and structure. Major aims in the synthetic strategies are (1) to tailor the band gap in semiconductor materials and (2) to achieve high carrier concentration and mobility in the conductive materials. Present emphasis is on two-dimensional networks, such as those related to graphite. Electron oxidation of such materials (with accompanying intercalation to form salts) generates durable and conductive materials (some conducting better than aluminum). The layered materials can often be oxidized (and intercalated) electrochemically in reversible processes and some (e.g., $C_xF_{1-\delta}\cdot\delta HF$) may find use in high-energy electrodes. Physical chemical studies are being applied to such materials to determine the structure and bonding changes that accompany oxidation and reduction. Salts that are either proton conductors or fluoride-ion conductors, and that are resistant to oxidation but are not metallic, are being sought as solid electrolytes for use with the metallic-layer-material salts. [4.5 FTE]

99. *Catalytic Hydrogenation of Carbon Monoxide*

A.T. Bell, G.A. Somorjai

The purpose of this project is to develop an understanding of the fundamental processes involved in catalytic conversion of carbon monoxide and hydrogen to gaseous and liquid fuels. Focus is on defining the factors that limit catalyst activity, selectivity, and resistance to poisoning, and the relationship between catalyst composition/structure and performance. Surface diagnostic techniques (LEED, AES, XPS, EELS, IRS, TPD) are used to characterize supported and unsupported catalysts before, during, and after reaction. The information thus obtained is combined with detailed studies of reaction kinetics to elucidate reaction mechanisms, and the influence of modifications in catalyst composition and/or structure on the elementary reactions involved in carbon monoxide hydrogenation. [6.0 FTE]

100. *Transition Metal Catalyzed Conversion of CO, NO, H_2, and Organic Molecules to Fuels and Petrochemicals*

R.G. Bergman

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

101. *Formation of Oxyacids of Sulfur from SO_2*

R.E. Connick

The primary focus of the research is the fundamental chemistry of sulfur species formed from sulfur dioxide in aqueous solution and the reactions of these species. The chemistry of these species is of particular importance in the problems associated with atmospheric pollution by sulfur dioxide and the resulting formation of acid rain. Recent research has elucidated the kinetics of the exchange of oxygen atoms between bisulfite ion and water, using the nuclear magnetic resonance of ^{17}O for following the reaction. The kinetics of the oxidation of bisulfite ion by oxygen is being studied. Work remains to be done on the latter project and additional oxidation–reduction reactions of bisulfite should be investigated. Of particular interest are such reactions involving two or more oxidation states of sulfur itself (e.g., reactions involving HSO_3^-, H_2S, S_8, and the polythionates). A secondary goal is to determine factors controlling the rate of substitution reactions in the first coordination sphere of metal ions. Computer modeling of such systems is under way and some results for a two-dimensional model have been published. The work is being extended to three dimensions. [1.5 FTE]

102. Synthetic and Physical Chemistry
W.L. Jolly

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

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

The project objective is to design and synthesize novel organometallic compounds that exhibit new properties as potential catalysts in reactions to be used in the conversion of simple organic structures of industrial importance. In addition, the aim is to specifically construct new molecules that may activate organic chemicals to new reactions and that by virtue of their unusual topology and/or electronic makeup may be important new materials, such as photostorage devices, photocatalysts, and conductors. Recent work has centered on the novel and unusual behavior of oligocyclopentadienylmetals, which has led to the discovery of unprecedented bi- and trinuclear chemistry of homo- and heteronuclear transition metal derivatives. Several of these compounds have shown novel and distinct transformations relevant to catalysis, surface reactions, and photochemical storage cycles. Work on fulvalene dichromium, molybdenum, tungsten, and ruthenium and their mixed heterodinuclear analogs has uncovered (1) new binuclear modes of hydrogen evolution from dihydrides, (2) chemo- and regiospecific catalytic hydrogenation of 1,3-dienes and carbon monoxide, (3) carbon–carbon bond formation through biscarbenes, (4) the occurrence of unprecedented mechanisms of photosubstitution, and (5) the utilization of photochemically activated complexes in thermal processes. [3.5 FTE]

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Isotope and Nuclear Chemistry Division $296,000

104. Transition Metal Mediated Reactions of SO_2
G.J. Kubas, R.R. Ryan

The objective of this project is to delineate the basic chemistry of SO_2 reactions mediated by transition metal complexes, particularly the mechanistic aspects of catalytic or potentially catalytic conversions of SO_2 to harmless products such as sulfur. Homogeneous catalytic reduction of SO_2 by hydrogen using catalysts such as molybdenum sulfide complexes is being studied to determine reaction rates, mechanisms, and catalyst stability to oxidation or sulfidation. Metal sulfide catalysts have been chosen to circumvent the latter problem and because of their use in hydrodesulfurization processes. Heterogeneous catalytic conversions of SO_2 will be carried out in order to determine potential applications for SO_2 emission control. Homogeneous reduction of nitrogen oxides both in the presence and absence of SO_2 is also being studied. Another facet of our work involves oxygen transfer reactions of SO_2 that are of potential relevance to atmospheric oxidation of SO_2 to SO_3. We have recently observed that certain metal complexes promote SO_2 disproportionation to SO_3-containing moieties and will explore the mechanisms of these processes further. Activation of the H–H bond in hydrogen is also being investigated in complexes that contain the first examples of molecular hydrogen coordination. Electronic control of dihydrogen vs. dihydride coordination and tautomeric equilibrium between these two forms are being studied in order to map out the reaction coordinate for H_2 addition to metals. [1.75 FTE]

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Chemical Technology Division $490,000

105. Kinetics of Enzyme-Catalyzed Processes
E. Greenbaum, J. Woodward

This project focuses on the physicochemical mechanisms of artificial photosynthetic systems including: (1) the reconstituted *in vitro* system composed of isolated spinach chloroplasts, ferredoxin, and hydrogenase (CFH) and (2) the substituted systems in which nonbiological catalysts are electronically linked to water splitting and chloroplast-reducing power. Research on the fundamentals of stabilization and immobilization of cellulase is also performed. Colloidal platinum has been prepared and precipitated directly onto chloroplast photosynthetic membranes. This system is capable of the simultaneous photoevolution of hydrogen and oxygen. Experimental data support the interpretation that part of the platinum metal catalyst is precipitated adjacent to the photosystem I reduction site of photosynthesis and that electron transfer occurs across the interface between photosystem I and the catalyst. A photoelectrochemical cell composed of filter-paper-entrapped platinized chloroplasts has been constructed. Sustained photocurrents and photovoltages were measured using continuous polychromatic illumination. The sign of the measured photovoltage is consistent with the prevailing vectorial photochemical model of photosynthesis. Separation and purification of cellulase isoenzymes have been achieved. [4.0 FTE]

Chemistry Division **$2,395,000**

106. Organic Chemistry and the Chemistry of Fossil Fuels

A.C. Buchanan, B.M. Benjamin, L.L. Brown, E.W. Hagaman, R.R. Chambers, F.M. Schell

The project objective is to gain new information at the molecular level concerning the organic chemical structure and reactivity of coals. Structurally diagnostic organic reactions are developed and used to quantify specific structural features of coals. Focus is on ^{13}C and ^{14}C double labeling techniques, solid-state ^{13}C NMR, and parallel studies with model compounds. Acid-catalyzed transalkylation chemistry is being used to probe aliphatic substituents and linking groups in native coals, coal extracts, and coal products. Acidic O–H and C–H sites in coal are being quantitatively probed by reactions with bases of well-defined strengths. Emphasis is on the use of carbanion bases to further assess the importance of five-membered-ring hydroaromatic structures in coals. Solid-state NMR techniques are also being developed, particularly for use with selective chemical modifications in the study of coal structure. Current emphases are the development of ^{1}H–^{31}P–^{13}C double cross polarization techniques, and the use of CP/MAS–^{13}C–NMR to estimate the number of chemically reactive, acidic methylene and methine carbon centers in bituminous coals. Reaction mechanisms that underlie the thermal reactivity of coal are also being investigated. The thermal reaction pathways for surface-attached 1,3-diphenylpropane are being probed to further examine the impact of restricted mobility on free-radical reactivity. Information derived from these fundamental studies will contribute to the knowledge necessary for developing novel processes for the use of coal as a source of liquid fuels and chemicals. [8.2 FTE]

107. Basic Aqueous Chemistry to High Temperatures and Pressures

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

The purpose of this project is to conduct experimental research on reactions and thermodynamic properties of important classes of solutes in water at high temperatures and pressures. Systems under study often have immediate applicability in energy-related technologies, but always form a basis for evaluating theoretical models that can advance understanding and predictability of chemical reactivity. Topics include thermodynamic properties of (single and mixed) electrolytes and nonelectrolytes in addition to equilibrium and kinetic studies providing enthalpies, volume changes, and equilibrium constants for reactions such as ion association, acid and base ionization, complexation, oxidation–reduction, hydrolysis, and solubilities in aqueous solutions. Progress depends on continuing development of new apparatus and techniques to complement existing capabilities. Research is conducted with a high level of precision on real systems selected for their practical and fundamental significance. Experimental capabilities include flow calorimetry, isopiestic and electrochemical measurements, electrical conductivity, vibrating-tube densimetry, and Raman and ultraviolet-visible spectrophotometry to extremes of temperature and pressure. Results have application in steam generation, nuclear and chemical waste disposal, chemical processing, the extraction of heat and material resources, and basic hydrothermal geochemistry. [4.9 FTE]

108. Heterogeneous Catalysis Related to Energy Systems

S.H. Overbury, D.R. Huntley

This project involves two related activities. In the first, the technique of low-energy alkali ion scattering as a surface-specific structural tool is being developed and applied to the study of clean and adsorbate-covered surfaces of catalytic interest. Comparison of the experimentally observed energy and angle dependencies of the scattered ions with computer simulations allows for quantitative descriptions of surface structure. These methods have been applied to study: (1) bonding geometry and ordering of oxygen, carbon, nitrogen, and sulfur overlayers on Mo(001) and Mo(111); (2) surface structure of amorphous Fe-20% B ribbons; (3) surface layer relaxations on Mo(111); and (4) the structure of carburized Mo(111) and W(100) surfaces. The second activity focuses on studying the surface adsorption and reactions of organosulfur molecules and hydrogen on single crystal metal surfaces in ultrahigh vacuum. Electron energy-loss spectroscopy and thermal desorption spectroscopy are used to characterize the resulting surface species in order to elucidate mechanistic details of desulfurization reactions. Ultimately, the sample will be moved to an adjoining cell that will be used for sample treatments and for monitoring hydrodesulfurization reactions over a wide pressure range. Measured reactivity and selectivity will be correlated with changes in the surface composition and structure. [2.4 FTE]

109. Molten Salt Catalysts for Clean Fuel Synthesis

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

This research is directed at mechanistic aspects of molten salt catalysis and at the stabilization and characterization of reactive organic intermediates in these unusual media. Current research is centered on Friedel-Crafts catalysis in liquid chloroaluminates with high $AlCl_3$ activity and, in particular, on the respective roles of Bronsted and Lewis acidity in ionic liquids in which $Al_2Cl_7^-$ is the predominant anion. The Bronsted acidity of molecular HCl in such melts is being investigated by spectrometrically measuring the degree to which it protonates arenes to form arenium ions. Although these arenium ions are highly reactive in most media, they are for the most part quite stable in these $Al_2Cl_7^-$-rich liquids. Studies are also being made of the sigma complexation of arenes and other bases by $AlCl_3$ in the absence of protic sources. This study utilizes spectroscopic and electroanalytical methods. In general, these investigations are possible only with liquid chloroaluminates of exceptional purity. [3.4 FTE]

Pacific Northwest Laboratory
Richland, Washington 99352

Chemical Sciences Department **$565,000**

110. Free-Radical Chemistry of Coal

J.A. Franz, M.S. Alnajjar

This project focuses on determining the energetics and mechanisms of free-radical reactions related to thermal dissolution of coal in hydrogen donor media. Relative rates of radical rearrangements, atom-transfer reactions, fragmentation reactions, and charge-transfer reactions are being determined; absolute rates are determined by kinetic laser flash spectroscopy for key atom-transfer reactions. Novel hydrogen transfer and initiation pathways involving radical hydrogen transfer are being examined theoretically, using semiempirical and *ab initio* approaches; and the kinetics of hydrogen transfer from cyclohexadienyl radicals to aryl structure are being examined. Atom-transfer reactions of sulfur-centered radicals and the intermediacy of hypervalent sulfur radicals are under study. Carbon–sulfur bond-making and -breaking reactions and sulfur-centered radical intermediates are being studied. [2.5 FTE]

111. Thermolysis Mechanisms of Lignocellulosic Materials
D.A. Nelson

The purpose of this research is to define the fundamental reaction mechanisms involved in the conversion of lignocellulosic material to new compounds. Products from cellulose, lignin, hemicellulose, and protein or respective chemical models are investigated over a range of conditions, including temperatures up to 350°C. The alkaline cleavage of lignin models proceeds through an internal displacement of the aryloxy group to provide an epoxide intermediate that opens to a glycol. The observed rate of reaction was found to be sensitive to steric bulk and polar substituents in the orthoposition of the aryloxy ring. A key model of lignin, containing a thiol group, was prepared and was found to undergo photolytic fragmentation. The product mixture of this reaction suggests the intermediacy of a free-radical pathway. Phase-transfer catalysis has been found to be an excellent procedure for isolating intermediates during the alkaline cleavage of lignin. [1.0 FTE]

Sandia National Laboratories
Albuquerque, New Mexico 87185

Surface Science Division **$386,000**

112. Surface Catalytic Studies
D.W. Goodman

The goal of this research is to develop an understanding of surface-catalyzed reactions at the molecular level using the full complement of modern surface analytical techniques. Of primary importance are those reactions relating to the synthesis of hydrocarbons from H_2 and CO. The experimental work includes the determination of reaction kinetics of hydrocarbon formation and rearrangement over single crystal catalysts. The work is carried out in a custom-built ultrahigh vacuum apparatus allowing both kinetic measurements and surface analysis. Recent studies have provided unique information regarding the mechanisms of important catalytic reactions over transition-metal surfaces. Reactions studied include methanation, alkane hydrogenolysis, alkane dehydrogenation, and alkene hydrogenation. Focus is on (1) the relationship of surface structure and activity toward breaking carbon–carbon bonds, (2) the critical metal-atom ensemble sizes required for catalytic activity, and (3) promotion of catalytic properties through alloying or impurity modification. Recent work has shown that unique catalytic behavior can be obtained by combining elements on a solid surface such that the overlayer metal, which is mismatched to the substrate, grows pseudomorphically with respect to the substrate. These strained-metal overlayers are exciting new materials with novel catalytic properties. For example, submonolayer amounts of copper on the Ru(0001) surface yield catalytic properties that are not like those of copper or ruthenium but exhibit greatly improved behavior for certain reactions. This project uses an array of surface techniques including Auger spectroscopy, x-ray and ultraviolet photoemission spectroscopy, temperature programmed desorption spectroscopy, and electron energy-loss spectroscopy. [2.0 FTE]

Solar Energy Research Institute
Golden, Colorado 80401

Solar Fuels Research Division **$225,000**

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

This project involves the synthesis and characterization of new inorganic and organometallic complexes and their evaluation as catalysts for the conversion of substrates, such as CO_2 and CO, to fuels and chemicals. Current focus is on the reduction of CO_2 and CO using two different approaches. In one approach, bimetallic metal hydrides generated by hydrogenation reactions of early transition metal alkyl complexes react with CO_2 and CO to form formaldehyde and well-defined oxidized metal complexes. Efforts are under way to determine whether these processes can be made catalytic, and to study the influence of various metals on these reactions. A second approach is the development of redox catalysts that mediate the electrochemical reduction of CO_2 and CO. In such processes the catalyst is reduced electrochemically. The reduced catalyst is then responsible for the reduction of substrate molecules. A new class of palladium complexes containing tridentate phosphine ligands has been synthesized, and is capable of mediating the electrochemical reduction of CO_2 to CO. Mechanistic studies of these catalysts are in progress. Similar studies are proposed for the electrochemical reduction of CO. The overall objectives of this research are to increase our knowledge of the fundamental transformations involved in catalytic systems and to develop new catalysts for fuel production processes. [1.6 FTE]

Separations and Analysis

Ames Laboratory
Iowa State University
Ames, Iowa 50011

Processes and Techniques Program **$1,050,000**

114. Analytical Spectroscopy
V.A. Fassel

This project entails systematic observation of spectroscopic phenomena in order to derive new spectroscopic analytical concepts that offer promise of solving singularly difficult analytical problems in the various fields of energy generation (e.g., conversion of coal to liquid and gaseous fuels, recovery of shale oil, solid-state materials research, and environmental pollution assessment). Emphasis is on: (1) novel applications of electrical plasmas as vaporization-atomization-excitation-ionization sources for analytical atomic emission, mass, and fluorescence spectroscopy; (2) analytical applications of highly selective energy transfer from energetic, long-lived species to trace level organic or inorganic constituents leading to optical emission; (3) use of processes developed in (2) to devise noble-gas afterglow, GC or LC detectors for element-specific, multielement speciation at trace concentration levels; and (4) photoacoustic and thermal wave-imaging processes and their analytical applications. [2.7 FTE]

115. Analytical Separations and Chemical Analysis
J.S. Fritz

A major effort is under way to improve methods of ion chromatography and liquid chromatography of metal chelates, so that complex mixtures of inorganic anions and cations can be separated and analyzed with the same facility that is possible in organic chromatography. Research in ion-exclusion chromatography is designed to improve understanding of the principles and to create methods for determining hydrophilic molecular compounds. Research on ion-exchange resins is designed to provide better resins for chromatography and to give a better understanding of the important scientific problem of resin selectivity. New methods are being developed for the selective concentration of various organic compounds prior to chromatographic analysis. Improved statistical theories of chromatography are being formulated to correct some inadequacies of prevailing theories and provide a better foundation for chromatography. [2.7 FTE]

116. Mass Spectroscopy in Chemical Analysis
R.S. Houk

The general objective of this project is to develop, evaluate, and characterize ionization techniques with potential value for analytical mass spectrometry (MS). Current efforts concentrate on improving techniques for extracting and mass-analyzing ions from inductively coupled plasmas (ICPs). The value of this ion source for elemental and isotopic analysis of solutions on a rapid, direct basis is being demonstrated. Various alternate techniques for introducing samples are being studied with the ICP-MS device as an element-selective, isotopically sensitive detector. These sample introduction methods include electrothermal furnaces or arc discharges for direct vaporization of solids and liquid chromatographic separations for determining elemental speciation via isotopic tracing experiments. Mass spectra of polar, nonvolatile organic compounds can be obtained directly from aqueous solutions, provided ICP conditions are properly cooled. Temperatures, ion and electron densities, and energy-transfer processes in ICP are being modeled and studied experimentally. Ionization techniques for mass spectrometric analysis of solids are also investigated. These techniques include a laser probe for direct, absolute elemental analysis and a pulsed neutral atom beam for desorption and ionization of nonvolatile organic molecules. [2.7 FTE]

117. Chemical Analysis at Liquid–Solid Interfaces
M.D. Porter

This project focuses on new strategies for characterizing and controlling the structure and reactivity of thin polymeric and monomolecular films at liquid–solid interfaces. One activity involves novel spectroscopic and electrochemical techniques for the *in situ* characterization of the structure and reactivity of thin molecular films at metal and semiconductor interfaces. At present, a methodology based on Fourier transform infrared reflection spectroscopy and high-sensitivity thin-layer spectroelectrochemistry is being studied to probe the composition and molecular arrangement (i.e., orientation, packing density, and coverage) of the aforementioned surface structures. The second activity examines the chemical and electrochemical reactivities of thin molecular films. Focus is on new approaches for constructing and applying these films as sensors for solution chemical analysis and as chemically modified electrodes for electrocatalysis. Current studies examine the utility (analysis selectivity and response time) of sensors fabricated by the chemical modification of porous polymer films. [1.0 FTE]

118. Lasers in Analytical Chemistry
E.S. Yeung

This project will develop new analytical techniques relevant to pollution monitoring, combustion diagnosis, and material evaluation in energy production. New spectroscopic concepts and instrumentation (particularly those involving lasers) are studied so that analytical methods can gain in sensitivity, selectivity, accuracy, and speed. Focus is on: (1) the development of the laser microprobe for atomic spectroscopy on surfaces; (2) new optical detectors for liquid chromatography suitable for complex organic samples; (3) nonlinear Raman methods and two-photon methods applied to analytical problems; (4) photoacoustic and interferometric concepts for improved absorption measurements, especially in flow systems; (5) high-resolution spectroscopy for stable isotope ratio determinations; and (6) laser-induced chemiluminescence for specific gas analysis. Investigations include the fundamental principles behind the measurements, evaluation of the analytical potentials, and demonstration of the analytical method in representative samples. [5.4 FTE]

Argonne National Laboratory
Argonne, Illinois 60439

Chemistry Division **$1,170,000**

119. Separations Science Related to Nuclear and Hydrometallurgical Technology
E.P. Horwitz

The project objectives are (1) discovery, characterization, and utilization of new organic extractants and aqueous-soluble complexants for the separation of metal ions and (2) elucidation of the basic chemistry involved. Major areas of investigation are: (1) development of new concepts in separation by complexation, (2) synthesis and characterization of new classes of solvent extractants for metal ion separation by liquid–liquid extraction, (3) spectroscopic and conformational studies of metal ion complexation by extractants, and (4) evaluation of the separation potential of new extractant systems with emphasis on new methods for by-product recovery from radioactive waste and new methods for the recovery of critical and strategic materials from low-grade domestic sources. [7.4 FTE]

120. Particle-Induced Desorption/Ionization Mass Spectrometry
J.E. Hunt

The importance of mass spectrometry in the analysis of high-molecular-weight "involatile" compounds has been growing steadily. In large part, this growth is attributable to the introduction of particle-induced desorption/ionization techniques. In particular, ^{252}Cf–PDMS has the potential to make a direct and significant impact on analyses of classes of compounds that have heretofore been considered intractable. Detection of ions produced by this technique has revealed amazingly large, intact ions such as proteins, nucleic acids, and small enzymes. Well-defined incident particle beams from accelerators have made detailed investigation into the mechanisms of desorption possible. The project objective is to understand the events underlying the desorption of molecular ions from a condensed-phase surface by the passage of a fast, heavy particle. The major concern of this research is to improve and extend the analytical utility of these desorption/ionization methods in the mass spectrometry of high-molecular-weight compounds by using well-characterized fast-atomic and multiatomic ion beams to study the effects of desorption from solid samples of known composition. Fission fragments from ^{252}Cf (in a ^{252}Cf-plasma desorption mass spectrometer) are also being used to study ion yields from monolayer and other well-ordered sample structures. [2.4 FTE]

Brookhaven National Laboratory
Upton, Long Island, New York 11973

Department of Applied Science **$525,000**

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

This project develops new analytical techniques for elemental determinations and chemical speciation using synchrotron radiation from the National Synchrotron Light Source (NSLS). Equipment is being designed to produce a focused monoenergetic x-ray beam with a spatial resolution in the neighborhood of 10 micrometers. Other apparatus has been assembled that uses a collimator with either monoenergetic x rays or white radiation to produce beams with sizes around 30 micrometers. The x rays from the NSLS have energies between about 4 and 20 keV, which will make possible investigation of all elements in the periodic table with $Z > 10$. Techniques for precise trace element measurements with minimum detectable limits approaching one part in 10^9 are being developed concurrently for both bulk and microanalysis. Chemical speciation will be achieved by use of precision x-ray energy measurements and electron spectroscopy techniques. A searching test of the new methods is made by comparison of the results obtained with synchrotron radiation with those obtained by other methods. These tests require the application of the techniques to samples obtained from a variety of energy-related fields. The use of synchrotron radiation for elemental quantification is supported by the use of nuclear ion-beam analysis, which makes available complementary analytical techniques that are used to corroborate and extend the synchrotron radiation results. [3.5 FTE]

122. Stationary-Phase Advances and Novel Detection Principles for Analytical Chromatography
S. Springston

This project focuses on improving separation capabilities in analytical chromatography through several parallel approaches. One approach seeks increased selectivity in capillary gas chromatography (GC) by preparing cross-linked stationary phases of varying polarity with *in situ* generated low-temperature plasmas. Plasmas appear uniquely suited for several different preparation steps including cleaning, deactivation, cross-linking of stationary phases, and modifying stationary-phase polarity. A second approach involves mesomorphic liquid-crystalline stationary phases, and anticipates selectivity improvements in condensed-phase separations (liquid and supercritical mobile phases). A third approach enhances column performance in liquid chromatography (LC) by isolating uniform particle-size fractions of silica-based packing material ranging from 1 to 2 μm. Packing techniques will be studied. Peak asymmetry, column permeability, and column efficiency will be related to packing structure. A fourth approach seeks improved detection sensitivity for a wide range of chemical species. Radiolytic/photolytic reactions and energetic species coupled with various detection schemes (e.g., solvated electron capture, fluorescent excitation, chemiluminescent enhancement) will be investigated for LC and supercritical fluid chromatography (SFC). Computer modeling and optimization studies will support and coordinate advances in the above areas. [2.0 FTE]

Idaho National Engineering Laboratory
Idaho Falls, Idaho 83401

$145,000

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

This project studies two ionization processes for application to negative ion mass spectrometry: negative surface ionization and electron capture. Surface ionization studies focus on systems where the species of interest are chemisorbed on a low work function surface, followed by thermal desorption. Ionization efficiency has been increased by several orders of magnitude using this technique. This technology is currently used for the *in situ* study of catalysis mechanisms. A unique electron capture ion source using crossed electric/magnetic fields has been theoretically modeled, designed, constructed, and tested. Some of the negative ion species produced in this source spontaneously detach an electron after a few to tens of microseconds, and the properties of these types of negative ions are being studied to develop high-energy neutral particle beams. Studies are progressing in the computer modeling of the trajectories and reactions of ions in electrostatic lenses. [1.0 FTE]

Monsanto Research Corporation–Mound
Miamisburg, Ohio 45342

Operations Department **$340,000**

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

This project will investigate chemical exchange and liquid-phase thermal diffusion as techniques for stable isotope separation. The chemical exchange work is directed toward finding significant equilibrium isotope effects in metal isotope exchange reactions emphasizing macrocyclic complexants to develop two-phase isotope exchange processes for practical separations. The liquid thermal diffusion work is directed toward (1) further development of the recently discovered relationship between the elementary liquid-phase thermal diffusion effect and molecular mass and structure and (2) acquiring an improved understanding of the behavior of the liquid-phase thermal diffusion column and its application to the separation of stable isotopes. [3.2 FTE]

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Analytical Chemistry Division **$1,630,000**

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

This project involves the study of secondary ionization of organic compounds and resonant photoionization of sputtered atoms and small molecules. Physical and chemical interactions of various organic compounds dissolved in different matrices are related to the secondary ion mass spectrometry (SIMS) of such solutions. The focus is on finding matrices that enhance secondary ion emission for particular compound classes. A singular result of these studies is our finding that sulfuric acid solutions of polar-substituted polynuclear aromatic compunds (PACs) yield copious secondary ions characteristic of the dissolved PAC. These compounds are generally involatile, mutagenic, teratogenic, and carcinogenic, and their detection and identification is difficult when other techniques are used. In contrast, work with inorganic SIMS has involved resonance ionization to identify neutral particles sputtered from uranium and its oxides. This work has shown that the ratio of atomic neutrals to ions in the sputtered plume is quite sensitive to sample composition and surface contamination. Significantly reduced neutral populations were observed from the oxides as compared with the metal when the sputtering ion was argon. [1.9 FTE]

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

The focus of this project is in two main areas. The first area is the investigation of techniques to increase and improve the data that can be obtained from mass spectrometry/mass spectrometry (MS/MS). Current emphasis is on better understanding of the physical and chemical phenomena that occur in an MS/MS experiment and on designing new physical and chemical probes for this type of experiment. In particular, gas-phase ion–molecule reactions are being studied for their utility as chemical probes and as physical means of energizing gas-phase species. Energy transfer via nonreactive collisions is also being explored, to further elucidate the mechanisms involved in excitation via this method. The second main area of work is the study of gas-phase ionic reaction mechanisms. This work attempts to obtain a better understanding of the chemistry that occurs in the mass spectrometer, and complements the study of ion–molecule reactions mentioned above. As we learn more about the chemistry occurring in the mass spectrometer, the ability to identify unknown compounds from mass spectral data will be improved and the general understanding of basic chemical reactivity will be expanded. [2.6 FTE]

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

The purpose of this research is to investigate new spectroscopic tools for chemical and physical analysis. Three unique facilities at Oak Ridge National Laboratory (ORNL) are well suited to the current effort. The EN Tandem Accelerator and the Holifield Heavy Ion Research Facility are used for heavy-ion-induced x-ray satellite emission (HIXSE) studies; the Oak Ridge Electron Linear Accelerator (ORELA) provides an intense source of positrons that can be converted to monoenergetic state. Low-resolution measurements of HIXSE spectra have shown strong correlations to electronic structures of solids. The method can distinguish between metallic bonding in alloys and covalent–ionic bonding in compounds. A high-resolution spectrometer is being built to make more precise measurements that will allow more fundamental understanding of the structure of solids. Positron spectroscopy is a valuable tool for the study of surface and bulk properties of solids. The retrofitting of the ORELA for dispensing slow positrons is 85% complete. Initial uses of the beam will be in new types of mass spectroscopy studies, stimulated ion desorption, positron diffraction, and biological mutation experiments. The facilities developed in this project will be useful to institutions outside ORNL. [2.2 FTE]

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

The objective of this work is to advance the state of the art in spectrochemical analysis. Emphasis is on high-resolution optical spectroscopy and considerations of high sensitivity. Measurements with high specificity and sensitivity are being developed, based upon laser excitation. All aspects of the measurement are being considered (i.e., optical source, sample preparation, and type of spectroscopy). Various types of nonlinear optical spectroscopy are being explored, such as degenerate four-wave mixing and saturation spectroscopy. Both high- and low-pressure sample reservoirs are being studied. New types of tunable dye laser sources are being developed that employ photorefractive optical elements. Novel refractive index detectors for liquid chromatography and flow injection analysis are being considered. These detectors are based upon two-wave mixing in photorefractive materials. [3.2 FTE]

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

The project goal is to improve isotopic ratio mass spectrometry and to expand its areas of application. Improvements in instrumentation and methodology are sought that lead to better precision and sensitivity and enhanced specificity. Isotope dilution is extensively used to provide quantitative results. A class-100 clean room is used for preparation of small samples and study of low-level separations techniques. One major area of emphasis is resonance ionization mass spectrometry (RIMS). The ultimate objective of this work is to develop an analytical instrument that produces reliable isotopic ratios free of interferences. We are presently investigating the details of the physical processes underlying resonance ionization. Another significant area is new methodology for isotopic analysis of a wide variety of elements. We have adapted an isotope ratio mass spectrometer to perform analyses of krypton and xenon to precisions better than 0.01% RSD. Techniques for calcium and nickel also have been studied. [2.3 FTE]

Chemical Technology Division **$1,350,000**

130. *Chemical and Physical Principles in Multiphase Separations*
C.H. Byers, J.S. Watson, T.C. Scott, J.J. Perona

This project comprises several fundamental studies that address the issue of efficiency of energy utilization in separation processes. Focus is on improving mass transfer in liquid–liquid solvent extraction and on the use of external fields to improve fluid–fluid and solid–fluid separation systems. Enhancement of mass transfer rates in extraction is produced through the use of pulsing electric fields. Investigations in this area include mechanics of droplet oscillation, hydrodynamics of the droplet–continuum system, and mass transfer studies. Imposing an electric field upon droplet formation devices allows for increased control of the size of droplets formed. Theoretical analysis is under way to determine the energy input by the field and to predict droplet sizes. AC and DC fields are also used to study stabilized expanded beds of solids. Studies have been undertaken on liquid–solid and gas–solid systems that yield well-characterized, uniform-bed expansion. These studies are directed towards better understanding of hydrodynamic and mass transfer phenomena that occur in expanded particle systems. [4.2 FTE]

131. *Interactions of Solutes, Solvents, and Surfaces: Adsorption and Supercritical Extraction*
H.D. Cochran, J.S. Watson

This project combines experimental and theoretical investigations of molecular interactions between dissolved and adsorbed solutes with surrounding solvents and surfaces. The studies provide needed insight into the interactions important to separations by adsorption and in high-pressure systems, such as supercritical extraction operations. A new surface acoustic transmission technique is being developed that allows measurements of adsorption dynamics even at very high rates. The technique is potentially useful over a wide range of pressures including high pressures such as those necessary for supercritical studies. Systems chosen for experimental study are transition metal fluorides (MoF_6, UF_6) as solutes, CF_4 solvent, and fluorided quartz surfaces. These materials were selected because of their scientific and potential technical importance. The metal fluorides provide an opportunity for evaluating theoretical models for interactions in dense gases in the critical region. By studying different inorganic fluorides, one can vary the mass and volume of the solute molecule independently over a wider range than possible with more conventional organic systems. Many of these metal fluorides also are important in nuclear materials processing; improved understanding of their behavior at high pressures will have additional benefits. [2.8 FTE]

132. *Chemistry of Actinides and Fission Products*
L.M. Toth, D.J. Pruett, S.A. Sherrow

This project is concerned primarily with the fundamental chemistry of the actinide and fission product elements. Specific areas currently under investigation include: (1) spectroscopy and photochemistry of actinides in low-temperature matrices, with particular emphasis on isotope effects; (2) small-angle scattering studies of hydrous polymers in aqueous and nonaqueous solvents; (3) characterization of the structures and properties of pure and mixed actinide polymers; (4) photochemical studies of uranium, neptunium, and plutonium in aqueous solution; (5) kinetic and thermodynamic studies of complexation and redox reactions in aqueous and nonaqueous solutions; (6) determination of solvation numbers in aqueous and nonaqueous solutions; (7) properties of complexes with macrocyclic ligands; (8) development of inorganic ion exchange materials for actinide and lanthanide separations; and (9) studies of fundamental properties of aqueous and nonaqueous solvent systems in support of these primary fields of investigation. Special efforts are also made to develop research programs in collaboration with universities and industry. In this way, outstanding scientists and students are able to take advantage of the unique research facilities available at Oak Ridge National Laboratory, while the overall scope and quality of the project is enhanced. [2.3 FTE]

Chemistry Division **$850,000**

133. *Chemical and Structural Principles in Solvent Extraction*
B.A. Moyer, C.F. Baes, Jr., J.H. Burns, W.J. McDowell

This project uses a multifaceted approach to understanding the contribution of molecular structure and bonding to the selectivity, chemistry, and physical properties of solvent-extraction and related separation systems. Emphasis is on the use of macrocyclic coordinators as extractants or as extraction synergists; promising separation systems are identified by the application of relevant molecular-design criteria and by systematic extraction testing. Selected systems are then studied in detail to elucidate the thermodynamic and structural principles underlying the separation. Techniques used include: (1) measurement of extraction data as a function of the compositional variables followed by computer-aided data analysis to identify the reactions involved; (2) osmometry to determine association of organic-phase species; (3) calorimetric measurements to determine heats and entropies of reactions; (4) x-ray diffraction of crystalline model compounds; (5) NMR, UV/vis, and FT infrared spectral measurements to probe the bonding and structural aspects of organic-phase complexes; and (6) molecular mechanics calculations to evaluate relative energies of various known and hypothetical species and to predict stable configurations. Insights gained through this approach are tested, refined, and exploited through the synthesis of innovative extraction reagents and subsequent development of novel separation systems of possible value to U.S. energy programs. [5.7 FTE]

Pacific Northwest Laboratory
Richland, Washington 99352

Chemical Sciences Department **$1,069,000**

134. *Analytical Mass Spectrometry Research*
R.L. Gordon, J.M. Kelley, D.M. Robertson, J.J. Stoffel(s), J.F. Wacker

This project advances knowledge and techniques to extend the application of mass spectrometry to problems in chemical and isotopic analyses. The project (1) elucidates physicochemical mechanisms responsible for efficient ion production, (2) obtains methods for the control of surface work function of ion sources, (3) studies techniques for application of mass spectrometry to real-time analyses, and (4) establishes new ionization techniques. Surface analysis establishes physical and chemical properties of surface ionization sources and identifies chemical pathways responsible for ion production. Real-time mass spectrometry uses novel ion sources, mass separators, and ion detectors to develop direct particle sampling and measurement methods. Laser-assisted negative ionization is being studied as a gentle technique for large organic molecules. [2.6 FTE]

135. Fundamental Phase Partitioning in Supercritical Fluid Chromatography

R.D. Smith, C.R. Yonker

The goal of this project is a fundamental understanding of the kinetic and thermodynamic constraints upon partitioning of a solute between a supercritical fluid and a condensed or supported phase. In the most general sense, this project is exploring supercritical fluid phenomena in order to bridge the gap between understanding the gas and liquid states. The project involves investigation of fluid-phase reactivities, solubilities, and phase-partitioning kinetics relevant to supercritical fluid chromatography and extraction phenomena. Phase partitioning and related chromatographic processes are being studied using direct fluid injection-mass spectrometry, classical equilibrium sampling, and solvatochromic techniques. The focus is on gaining an understanding of chromatographic processes for polar and mixed supercritical fluid and solute systems and the kinetic and thermodynamic limitations upon separations in supercritical media. Both normal and reverse micelle systems, where the nonpolar phase is a supercritical fluid, are also being investigated as the basis for new separation methods. Experimental results are being compared with theoretical methods for prediction of fluid phase solubilities and actual chromatographic separations for model systems, to identify critical parameters for developing improved separation systems. [1.6 FTE]

136. Analytical Atomic Absorption Spectrometry Research

D.L. Styris

This project elucidates experimentally the mechanisms that control sample vaporization in graphite furnaces such as those used in furnace atomic absorption (FAA) spectrometry. Vaporization models obtained from these results provide understanding of chemical treatment and furnace effects, and thus establish the basis needed to help broaden and improve application of contemporary FAA spectrometric analysis and other spectrometries that incorporate graphite furnaces. 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. Pyrolytic graphite furnaces are used in this work; element vaporization that occurs in the presence of important stabilizers (e.g., palladium) is being investigated. The experimental technique is also being used to verify theoretical models of vaporization (e.g., vaporization of aluminum and the influence of magnesium as a stabilizer) and to elucidate mechanisms responsible for interferences among Group IIA elements. [1.3 FTE]

137. Laser-Based Analytical Techniques

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

The project objective is to design and evaluate laser-based analytical techniques for the detection and measurement of trace substances related to energy research and production. The current focus is a sensitive measurement method for noble gas isotopes. Typical concentrations of isotopes of interest are 10 to 12 orders of magnitude lower than for other isotopes of the same element. For example, ^{85}Kr is an effluent from nuclear facilities. Its normal concentration varies considerably but is on the order of 10^{-11} times that of the naturally occurring krypton isotopes. Our analysis has indicated the possibility of measuring such minute concentrations of noble gases by the photon-burst method, which we have demonstrated on alkaline earth elements. The analysis will require exciting the noble gas atom to an electronic metastable state that serves as the lower state of a two-level system. We have recently demonstrated a dc discharge method of creating the metastable state and have measured the isotopic splittings for stable krypton isotopes in the two-level transition. We are also developing the means to use inexpensive diode lasers for the photon-burst analysis. [1.5 FTE]

Chemical Engineering Sciences

Lawrence Berkeley Laboratory
University of California

Berkeley, California 94720

Applied Science Division **$319,000**

138. Turbulent Combustion

L Talbot, R.K. Cheng

The interaction between turbulence and chemical reactions in premixed and nonpremixed turbulent combustion flows is studied experimentally using laser diagnostic techniques. A theoretical study of premixed turbulent flames using the vortex dynamics method is also being conducted. The objectives are to obtain a better fundamental understanding of the turbulent combustion processes and to develop a theoretical model capable of predicting these processes. Four idealized experimental flow configurations are used: (1) heated wall turbulent boundary layer capable of supporting combustion in fuel-lean mixtures, (2) rod-stabilized turbulent v-flame, (3) Bunsen-type conical turbulent flame, and (4) turbulent flame stabilized by a stagnation plate. The nonpremixed turbulent jet flame burner is being designed and constructed. Statistical data of the temporal fluctuations of scalars and velocity in the v-flames and in the stagnation flow stabilized flames have been obtained. Linear array Rayleigh scattering (LARS), which measures instantaneous density profiles, was used to study flame movement. The flame passage time frequencies and the intermittency spectra were measured using a Mie scattering technique. Results are compared with the velocity spectra obtained for the velocity components normal and tangential to the flame brush. A deterministic theoretical simulation of the v-flame has been developed. Results show that the inclusion of vorticity generation is essential for proper modeling of premixed turbulent flame propagation. [3.0 FTE]

Materials and Chemical Sciences Division **$156,000**

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

Phase equilibria are required for efficient design of large-scale separation processes (e.g., distillation and extraction) in the chemical and related industries: processes that make optimum use of raw materials and conserve energy. Since the variety of technologically important fluid mixtures is extremely large, it is not possible to obtain all desired equilibria from experiment. Therefore, the objective of this research is development of molecular thermodynamics for interpretation and correlation of selected data toward reliable general prediction of phase equilibria for engineering. The correlations are expressed through semitheoretical physicochemical models in a form suitable for computer-aided design. Particular attention is given to systems of primary interest in energy-related industries, especially those concerned with fossil fuels, fossil fuel–water mixtures, and agricultural products. Since most high-boiling fossil fuel sources are mixtures of very many components, new experimental methods must be developed to determine the approximate composition of the mixture (characterization) and new conceptual tools must be developed to provide a framework for quantitative description of the mixture's properties (continuous thermodynamics). Development of molecular thermodynamics calls for a combination of theoretical, computational, and experimental work, and for simultaneous awareness of progress in molecular science and of realistic requirements for engineering design. [2.2 FTE]

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Theoretical Division **$85,000**

140. Thermophysical Properties of Mixtures
J.J. Erpenbeck

The thermophysical properties of mixtures of particles interacting through the hard-sphere potential (and other simple interactions) are evaluated, using the equilibrium techniques of Monte Carlo (MC) and molecular dynamics (MD), as well as nonequilibrium molecular dynamics (NEMD). Properties under investigation include the equation of state and transport properties. The latter include mutual and self diffusion, shear and bulk viscosity, thermal conductivity, and thermal diffusion. Fundamental questions arising in the theory of fluids and fluid mixtures are addressed where numerical "experiments" seem appropriate. We also consider merits of the various numerical techniques in providing thermophysical properties. In order to evaluate the "synthetic" NEMD technique, we have compared the calculation of the self-diffusion constant using this technique with an MC-MD method based on the Green-Kubo formula. The system under study is a dense Lennard-Jones fluid. We find the MC-MD result, when extrapolated to the thermodynamic limit, to agree with the NEMD result, extrapolated to the thermodynamic limit and to the limit of vanishing driving force. Contrary to claims found throughout the literature, we find: (1) the NEMD results have a dependence on the number N of particles, which is at least as large as that for the Green-Kubo method; (2) the statistical uncertainties inherent in the Green-Kubo method are much smaller than those for the NEMD method; and (3) the NEMD method is beset by instabilities in the flow that occur for large enough driving forces. Moreover, the transitional values of the driving force decrease with increasing N. As a result, it is very difficult to extrapolate the NEMD calculations to the large N limit. The apparent insensitivity of the NEMD results to N (reported in earlier studies and widely accepted in the literature) is a small-system effect, at least for high density. [0.5 FTE]

Sandia National Laboratories
Livermore, California 94550

Thermofluids Division-8363 **$340,000**

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

This research develops turbulence prediction methods for application to flows with high Reynolds numbers and large heat release. Four distinct modeling approaches are under study, each focused on a particular aspect of reacting turbulence: (1) time-averaged turbulence closure procedures, because these methods are still the most well developed and provide the best interpretation of turbulent diffusion flames; (2) unsteady vortex dynamics, a procedure that provides detailed flame propagation in premixed systems of complex geometry; (3) stochastic simulation of flame propagation, a new procedure that defines flame propagation by a process of random exchange between pockets of burned and unburned reactants; and (4) direct numerical simulation, where no turbulence approximations are used. Emphasis is on understanding the detailed mechanisms of heat, mass, momentum, and species transport in the mixing region of reacting flows. Our primary objective is to develop models of reactive turbulence that will be used to interpret data obtained in experimental reactive turbulence programs at the Combustion Research Facility, supported by the DOE Office of Basic Energy Sciences, Division of Chemical Sciences. [2.0 FTE]

Heavy Element Chemistry

Argonne National Laboratory
Argonne, Illinois 60439

Chemistry Division **$1,395,000**

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

The project objective is to understand the electronic structures and chemical properties of the actinide elements. Each activity seeks to develop this understanding in ways that relate actinide properties to the solution of critical basic and applied problems in the nuclear fuel cycle and to other energy and materials research. Syntheses of stable and reactive actinide solids are combined with bonding, reactivity, and electronic structure determinations so that actinide solids can be tailored to optimize desired material properties. Research in spectroscopy, photophysics, and photochemistry (1) relates to DOE programmatic interests in identification and separation of transuranium ions and isotopes; and (2) focuses on higher valent, reactive compounds of neptunium, plutonium, and transplutonium elements. Focus is on developing models of the electronic structure of transuranium ions, in order to aid the interpretation of bonding and magnetic interactions. Dynamic and thermodynamic parameters that characterize oxidation–reduction and complex formation reactions of actinides in aqueous solutions are probed with state-of-the-art pulse radiolysis and stopped-flow methods. Such investigations provide the basis for modeling the energetics of actinide ion reactions in process chemistry and in the aquatic environment. [10.5 FTE]

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Materials and Chemical Sciences Division $1,280,000

143. Actinide Chemistry
N.M. Edelstein

The project objective is to study actinide materials to provide the basic knowledge necessary for their safe and economic use in present and future technology. The project includes preparation of new gaseous, liquid, and solid phases and studies of their physical and chemical properties. Techniques for characterization include x-ray diffraction, optical and vibrational spectroscopy, magnetic resonance, and magnetic susceptibility. Equilibrium and kinetic data for complex formation are measured. From these complementary studies, new insights into the structural and chemical principles of actinide compounds are obtained to design new synthetic schemes to produce new materials. A major aspect is the design and synthesis of sequestering agents for actinide ions. These compounds are intended for use in the treatment of actinide poisoning and for possible application in the treatment of spent reactor fuels. Preparative, structural, and physical studies of new types of organoactinide, related organolanthanide, and new actinide inorganic complexes are continuing. Studies on optical spectra of free ions and actinide ions in crystals are being pursued in order to understand their electronic structure. [15.0 FTE]

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Isotope and Nuclear Chemistry Division $330,000

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

We are continuing the investigation of Pu(IV) carbonate complexation by a spectrophotometric method involving citrate as a competitive ligand. In addition, redox moderators are under investigation for accurate determinations of the potentials of irreversible actinide (V)/(IV) redox couples in carbonate media. These results should permit calculation of the solubility of neptunium and plutonium under groundwater conditions. As a result of the availability of about 7 mg of ^{249}Bk, we have initiated a study of the spectroscopy and electrochemistry of berkelium in carbonate media. We are also involved in the preparation and characterization of some new berkelium solid-state complexes containing carbonate ions. For berkelium oxalate, we have prepared all of the lanthanide and actinide (neptunium through californium) oxalates and recorded the Raman and absorption spectra of these compounds. Included in this work is x-ray characterization of the transuranium oxalates. This work constitutes the first structural studies of berkelium and californium oxalates. Oxalates are an important class of compounds that are quite insoluble examples of oxygen donor ligands. These ligands are structurally and chemically similar to other strong actinide complexants such as carbonate, citrate, and humic acid. [0.8 FTE]

145. Actinide Organometallic Chemistry
A.P. Sattelberger, R.R. Ryan

The project objective is to explore fundamental aspects of actinide organometallic chemistry. Focus is on the synthesis, characterization, and reactivity patterns of three general types of early actinide (Th → Am) organometallic complexes. One type is actinide(IV) monomers that contain a single reactive site, e.g., (COT)(Cp*)AnR, where R is an alkyl or hydride ligand, COT is the cyclooctatetraene dianion, and Cp* is the pentamethylcyclopentadienide ligand. These have been prepared for An = Th, U and will ultimately provide thermodynamic and mechanistic information on small molecule insertions into actinide–alkyl and actinide–hydride bonds as a function of the actinide. We also study heterobimetallic complexes containing an actinide and a transition metal (or two actinides) held in close proximity by bridging ligands (e.g., phosphido or thiolato). Our goal is to modify traditional reactivity patterns associated with the transition metals by the neighboring actinide's oxophilicity and Lewis acidity. Some of the phosphido-bridged thorium-containing complexes prepared in our laboratory, e.g., $Cp^*Th(\mu\text{-}PPh_2)_2Pt(PMe_3)$, exhibit metal–metal bonding. A systematic extension of this chemistry to other early actinides is currently under way. Finally, we are investigating high-valent (+5 and +6) organometallic complexes of the *trans*-thorium elements. High-valent organoactinide complexes may enhance reactivity not found in traditional An(IV) systems. Thus far, we have developed chemical and electrochemical routes to a number of uranium(V) organometallic complexes, including $[Cp^*UCl_5]^{-1}$. [1.0 FTE]

Materials Science and Technology Division $120,000

146. Actinide High-Temperature Thermodynamics
P.D. Kleinschmidt, J.W. Ward

This research project measures the enthalpy and entropy of reaction of actinide compounds and gases by using the high-temperature gaseous effusion technique. The effort will concentrate on systems for which there are at present few measurements or for which the data appear to be unreliable. The systems include actinide fluorides, oxides, and oxyfluorides. A combination of precise second-law vapor pressure values with thermodynamic functions allows tabulation of heat capacity, heat content, and entropy data from 298 to 3,000 K. The experimental results on the thermochemical stability of gases and solids will be correlated with the stability of other actinide and nonactinide systems. The thermochemical stability of these species is used to determine their concentrations in preparative reactions, purification, and photochemical processes. [0.7 FTE]

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Chemistry Division	**$1,310,000**

147. Chemistry of Transuranium Elements and Compounds

O.L. Keller, J.K. Gibson, R.L. Hahn, R.G. Haire, G.F. Payne

This project focuses on unusual or unique f-orbital and relativistic bonding effects associated with the actinide region of the periodic table. Studies center on the heavy-element isotopes of Cm through Es available from the DOE National Transplutonium Production Program. We also study the chemistry of these heaviest elements in relation to the lighter actinides and the lanthanides. An example of f-orbital bonding effects is found in our characterizations of the pressures needed to bring about a transition of the 5f electrons in Am, Cm, Bk, and Cf from an atomic nonbonding condition to a metallic bonding condition. These extremely high pressure experiments on the pure metals are now being extended to alloys and compounds. In the area of solid-state chemistry and physics, we often select particular classes of compounds for study on the basis of their ability to indicate significant chemical differences between the lanthanides and the actinides. For example, the properties of the hydrides, pnictides, and chalcogenides are expected to differ significantly between the 4f and 5f electron series. Crystallographic, thermodynamic, and magnetic studies of such compounds are under way. Operation of a high-temperature Knudsen cell–mass spectrometer system will allow characterization of high-temperature, gaseous molecular systems. Unique compounds that might be stabilized under such extreme conditions include EsF_6 ($5f^7$ half-filled shell stabilization) and diatomic molecules (e.g., CfO and CfS). The development of accurate theoretical treatments of relativistic f-electron systems has been slow because of the inherent complexity. Characterizing gaseous diatomic compounds simplifies the molecular calculational problem to the greatest possible extent. We are also searching for unusual low oxidation states of the actinide elements by developing new types of electrolyte chemistry in selected high-boiling aprotic organic solvents. [8.4 FTE]

OFFSITE INSTITUTIONS

Photochemical and Radiation Sciences

University of Alabama
Tuscaloosa, Alabama 35487

148. Magnetic Resonance and Optical Spectroscopic Studies of Radiation-Produced Radicals
L.D. Kispert **$73,000**
Department of Chemistry

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

Alabama A and M University
Normal, Alabama 35762

149. Photoacoustic-Laser Spectroscopy of Halogens and Mixed Halogens for Energy Purposes
P. Venkateswarlu **$55,000**
Department of Physics

A photoacoustic spectrometer, including an electronic signal-averaging subassembly, has been designed and fabricated incorporating facilities for simultaneous recording of the sample absorption and the optogalvanic spectrum of neon for calibration. The photoacoustic spectrum of I_2(X-B transition) in the presence of atmospheric air has been recorded (16,040 to 19,800 cm^{-1}). Recording of a few bands under high resolution revealed partially resolved rotational structure. The photoacoustic spectrum of I_2 in the region 20,700 to 21,250 cm^{-1} (lying beyond the dissociation limit of the X-B transition) was analyzed as arising in the upper electronic states 1_g and 0_g^+ at T_e = 40,766 and 41,355 cm^{-1}, respectively, reached through two-photon absorption. Work on similar lines will be continued on ICl, IBr, and Br_2. Preliminary work on Br_2 showed photoacoustic absorption in the region 5,200 to 5,700 A. The vertical positions of the high-lying repulsive states of the halogen molecules that dissociate into $^2P_{3/2} + {}^2P_{1/2}$ atoms will be located by recording the photoacoustic spectra using the second harmonic of the tunable dye laser. This will establish the precise wavelengths of the solar radiation to be used for obtaining the halogen atoms in the $^2P_{1/2}$ state for the release of energy by transition to the ground $^2P_{3/2}$ state.

University of Arizona
Tucson, Arizona 85721

150. Mechanisms of Photochemical Energy Conversion by Chlorophyll
G. Tollin **$96,000**
Department of Biochemistry

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

Arizona State University
Tempe, Arizona 85287

151. Photoinitiated Electron Transfer in Multichromophoric Species: Synthetic Tetrads and Pentads
J.D. Gust, Jr., T.A. Moore **$105,000**
Department of Chemistry

The goal of this project is to design, synthesize, and study the photochemistry of molecules that produce long-lived high-energy charge-separated states with a high quantum yield when excited with visible light. Molecules are being prepared in which four or five chromophores such as carotenoid polyenes (C), porphyrins (P), chlorophyll derivatives, and quinones (Q) are linked together via covalent bonds. These molecules should achieve long-lived photoinitiated charge separation via multistep intramolecular electron-transfer reactions resembling those found in photosynthetic reaction centers. For example, molecules of the type C–P–Q–Q have been prepared, and their photochemistry is being investigated. Excitation of the porphyrin moiety leads to an initial charge-separated state $\mathrm{C{-}P^{+\cdot}{-}Q^{-\cdot}{-}Q}$, which is ultimately converted to a final state $\mathrm{C^{+\cdot}{-}P{-}Q{-}Q^{-\cdot}}$ · via two intermediate species: $\mathrm{C{-}P^{+\cdot}{-}Q{-}Q^{-\cdot}}$ and $\mathrm{C^{+\cdot}{-}P{-}Q^{-\cdot}{-}Q}$. The overall yield of charge separation is greater than can be obtained in related molecules that achieve a similar final charge-separated state with fewer intermediate electron-transfer steps.

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

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

Boston University
Boston, Massachusetts 02215

153. Study of Intermediates from Transition-Metal Excited-State Electron-Transfer Reactions
M.Z. Hoffman **$81,000**
Department of Chemistry

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

Brandeis University
Waltham, Massachusetts 02254

154. Photochemical Reactions of Complex Molecules in Condensed Phase
H. Linschitz **$88,700**
Department of Chemistry **(20 mo.)**

This project seeks to identify and evaluate factors governing the efficiency of primary radical formation in excited-state electron-transfer reactions. This is a general problem confronting photoredox energy conversion systems, since the same kinetic intermediates involved in energy-storing charge separation lead also to dissipative quenching. Triplet and radical extinction coefficients and yields are measured by laser-flash photolysis using aryl ketones and porphyrins as donor or acceptor substrates. In photoreduction of ketones or quinones by simple anions, radical yields increase markedly as anion concentration is raised far above quenching levels. Kinetic studies using mixed anion systems permit discrimination between singlet and triplet primary processes, and confirm that the high concentration effect involves reaction of a primary triplet charge-transfer exciplex with excess anion, forming a composite complex with low spin–orbit coupling. As models of photosynthetic reaction centers, ion-paired porphyrin "dimers" or aggregates have been prepared from oppositely charged monomers, and their optical, magnetic, and photophysical properties have been characterized. Mixed dimers containing different metals show biphasic decay of flash transients, suggesting charge transfer within a triplet porphyrin ion pair.

University of California
Irvine, California 92717

155. Research in Chemical Kinetics
F.S. Rowland **$227,000**
Department of Chemistry

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

156. *Single-Collision Studies of Hot Atom Energy Transfer and Chemical Reaction*
J.J. Valentini **$68,700**
Department of Chemistry

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

University of California
Los Angeles, California 90024

157. *Time-Resolved Laser Studies on the Proton Pump Mechanism of Bacteriorhodopsin*
M.A. El-Sayed **$120,000**
Department of Chemistry and Biochemistry

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

University of California
Santa Barbara, California 93106

158. *Energy Transformations in Organometallic Compounds*
R.J. Watts **$132,000**
Department of Chemistry

This project explores basic photochemical and photophysical phenomena in transition metal complexes. The primary areas of endeavor include: (1) photochemical and photophysical consequences of metal–carbon bonding to acceptor ligands with extended π 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 π conjugation in N-heterocyclic ligand–metal complexes; and (5) photophysics of mixed-valence solid-state materials. Techniques applied in these projects include time-resolved emission spectroscopy, laser-induced transient and excited-state absorption spectroscopy, and ^1H and ^{13}C NMR spectroscopy. Laser double resonance techniques are presently being developed with newly acquired excimer/dye lasers for the purpose of characterizing electronic relaxation between excited states of metal complexes. Synthesis and characterization of complexes containing metal–carbon bonds are carried out to facilitate the projects in area (1) above. The emission spectroscopy and photoinduced electron-transfer reactions of several of these complexes show them to be powerful photoreducing agents. Their participation in photoinduced electron-transfer reactions that are highly endergonic are presently under investigation.

Clemson University
Clemson, South Carolina 29634-1905

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

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

University of Colorado
Boulder, Colorado 80309

160. *Investigation of Redox Processes at Semiconductor Electrode/Liquid Junctions*

C.A. Koval **$140,000**
Department of Chemistry and Biochemistry **(19 mo.)**

Semiconductor electrode/liquid junction solar cells represent a versatile way to use solar energy because photon energy can be used to make electricity or chemical fuels, or can be used as a photocatalyst. Many fundamental questions regarding currents across these junctions remain unanswered. Thus we are making measurements analogous to those that were crucial for understanding this process at metal electrodes. Key aspects of our semiconductor studies are: (1) use of semiconducting materials that yield stable and reproducible interfacial energetics (InP and WSe_2); (2) use of both p- and n-type materials with a wide range of doping densities; (3) use of nonaqueous solvents to minimize surface corrosion processes; (4) thorough characterization of the interfacial energetics utilizing capacitance measurements; and (5) use of metallocenes as ideal solution redox probes. Studies with InP revealed that current flow was complicated by the presence of a surface oxide layer. To avoid this problem, p- and n-type WSe_2 single-crystal electrodes were prepared by chemical vapor transport. The WSe_2/acetonitrile junction appears to have nearly ideal electrochemical properties. An extensive set of current/potential curves has been obtained with these electrodes. This data set has several unique features and is presently being analyzed in detail.

Columbia University
New York, New York 10027

161. *Laser-Enhanced Chemical Reaction Studies*

G.W. Flynn **$110,000**
Department of Chemistry

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

Dartmouth College
Hanover, New Hampshire 03755

162. *Photoexcited Charge Pair Escape and Recombination*

C.L. Braun **$77,400**
Department of Chemistry

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

University of Florida
Gainesville, Florida 32611

163. *Radiation Chemistry of Hydrocarbon and Alkyl Halide Systems*

R.J. Hanrahan **$83,000**
Department of Chemistry

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

University of Houston
Houston, Texas 77004

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

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 couple this charge separation to chemical energy storage. Tetramethylbenzidine has been photoionized to produce the cation radical in liquid and frozen micellar solutions, and the photoionization is being optimized by surface modification of micellar systems. The cation is observed by optical absorption, electron spin resonance, and electron spin echo spectrometry. Nitroxide–water and nitroxide–alcohol interactions, detected by electron spin echo modulation analysis, with specific deuteration, indicate how micellar surface structure is related to the photoionization efficiency. Photoionization of chlorophyll in vesicle systems is also being investigated and optimized with specific electron acceptors. Electron spin echo modulation spectrometry has shown environmental differences between chlorophyll cations in vesicles and in glassy solutions.

Louisiana State University
Baton Rouge, Louisiana 70803-0301

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

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

Marquette University
Milwaukee, Wisconsin 53233

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

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

University of Massachusetts
Boston, Massachusetts 02125

167. Magnetic Resonance Studies of Photosynthetic Reaction Centers and Porphyrins
H. van Willigen **$95,700**
Department of Chemistry

The structure and photochemistry of photosynthetic reaction centers and model systems are studied with the aid of magnetic resonance techniques (ESR, ENDOR) and optical spectroscopy. Recent focus has been on the factors that affect photoinduced electron transfer from water-soluble porphyrins to acceptor molecules. The ESR and ENDOR signals from porphyrin cation radicals are used to study the kinetics of formation and decay of electron transfer products. ESR signals from porphyrin photoexcited triplets are used to obtain information on the yield of redox ion products. Systems investigated include anionic and cationic tetraphenylporphyrins, and porphyrin aggregates formed upon an admixture of oppositely charged porphyrins.

Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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

The long-range goal of this project is to establish principles and methods for efficient and inexpensive systems for optical to electrical or chemical energy conversion. Areas of study are: (1) semiconductor photoelectrode surface chemistry, (2) photoelectrode-confined polymer/catalyst assemblies, (3) catalysis of biological redox reagents, and (4) macromolecular reagents that effect rectification. Following the demonstration of strong interaction of RS^- and $R_2NCS_2^-$ with the II-VI semiconductors that leads to a large negative shift of the flat band potential, research has involved the interaction of CdS and CdSe with MoS_4^{2-} in solution. Interfacial capacitance studies show that such interactions improve the photovoltage for the II-VI semiconductors. Research of polymer/noble metal catalyst assemblies on p-type InP shows that the photocathodic evolution of H_2 can be dramatically improved in comparsion to the naked p-type semiconductor, as shown previously for p-Si and *a*-Si:H photocathodes. Synthesis and characterization of a decaalkylferrocene surface derivatizing reagent are under way to show that a hydrophobic surface can be prepared by surface modification. This may lead to new ways to make photoanodes durable in aqueous media. Functionalization of high-surface-area SiO_2 can be used to prepare a catalyst that allows the use of H_2 to rapidly reduce large biological redox reagents. Preliminary studies show that a very active hydrogenase can be equilibrated with surfaces bearing viologen-based redox reagents, which may enable the use of viologen/hydrogenase-modified photocathodes for the generation of H_2. Additional research concerns the characterization of macromolecular, multicomponent redox molecules that demonstrate that unidirectional electron transfer can be effected at the molecular level, duplicating one of the essential features of the natural photosynthetic apparatus.

University of Minnesota
Minneapolis, Minnesota 55455

169. *The Contribution of Electronically Excited States to the Radiation Chemistry of Organic Systems*

S. Lipsky **$85,000**
Department of Chemistry

Photophysical properties of organic molecules are being studied that have relevance in determining their behavior when subjected to high-energy radiation. Because the formation of ion pairs appears to be an important precursor of chemical damage in irradiated liquids, recent studies have concentrated on ion-pair properties. We generate these by photoionization of solutes in nonpolar liquids and observe their decay by (1) recombination (to give fluorescence) and (2) "escape" (to give photocurrent). These observations are made as functions of photon energy, nature of the solvent, concentration of electron scavenging impurities, and strength of externally applied electric and magnetic fields. Recently our efforts have been focused on the field effects. From electric field effects we can deduce the dependence on photon energy of the yield of ion pairs and on the average range of the ejected electron, which provides information about the nature of the ionizing transitions in these fluids. The magnetic field alters the yield of fluorescence by influencing the probability that recombining pairs are triplet or singlet. Since the ion pair is generated as a singlet, we thus deduce the rate of "thermalization" of spin momenta on the time scale of geminate recombination.

National Bureau of Standards
Gaithersburg, Maryland 20899

170. *Pulse Radiolytic Studies of Inter- and Intramolecular Electron Transfer Processes*

P. Neta **$134,000**
Center for Chemical Physics

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

University of Nebraska
Lincoln, Nebraska 68588-0304

171. *Electrochemical and Optical Studies of Model Photosynthetic Systems*

T.M. Cotton **$84,400**
Department of Chemistry

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

172. *High-Energy Halogen Atom Reactions Activated by Nuclear Transformations*

E.P. Rack **$82,000**
Department of Chemistry

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

University of North Carolina
Chapel Hill, North Carolina 27514

173. Energy Conversion Processes Based on Molecular Excited States

T.J. Meyer **$111,000**
Department of Chemistry

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

University of North Carolina at Charlotte
Charlotte, North Carolina 28223

174. Oligomer and Mixed-Metal Compounds, Potential Multielectron Transfer Agents

D.P. Rillema **$80,000**
Department of Chemistry

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

Northwestern University
Evanston, Illinois 60201

175. Intramolecular Electron-Transfer Rates

J.T. Hupp **$75,000**
Department of Chemistry

This project involves developing two new approaches for the direct assessment of thermal intramolecular electron-transfer rates. The first, based on new synthetic chemistry, makes use of preferential solvation to interconvert mixed-valence redox isomers of unsymmetrical binuclear metal complexes. A pulsed-accelerated-flow spectrophotometer, currently under construction, will be used for time resolution of the redox isomerization process. The second approach is based on light-induced (pulsed laser) metal-to-metal charge transfer in the near infrared, to create high-energy redox isomers, in mixed-valence complexes. Relaxation by electron transfer to create the low-energy isomers can be followed in the visible spectrum by transient absorbance spectroscopy. Two related experiments are electrochemical studies of site-to-site electronic coupling in multiple-site chemical systems and preresonance Raman studies of charge-transfer transitions. Results from the former experiment are being evaluated in terms of Mullikan charge-transfer theory. The latter experiment, which represents a novel application of recently developed theories of time-dependent vibrational spectroscopy, provides quantitative information about inner-shell reorganization energies.

Oregon Graduate Center
Beaverton, Oregon 97006-1999

176. Fundamental Studies in Oxidation–Reduction in Relation to Water Photolysis

J.K. Hurst **$106,100**
Department of Chemical and Biological Sciences

This project aims to improve our conceptual understanding of the influence of microphase separation and compartmentation upon oxidation–reduction processes. Three aspects are considered essential to developing practical "wireless" devices for solar photoconversion: (1) use of interfaces to promote charge separation and increase lifetimes of the initial redox products, (2) identification of mechanisms of transmembrane redox across bilayer membranes, and (3) development of regenerative cycles for water photolysis. We have developed systems for Zn(II) porphyrin photoreduction of N-alkyl-N′-methylbipyridinium(II) ions at the highly negatively charged interfaces of dihexadecylphosphate (DHP) vesicles with exceptionally high quantum yields (i.e., greater than 0.8) for formation of charge-separated products. The dissipative recombination reactions are strongly retarded by electrostatic repulsion, allowing opportunity for coupling to following reactions leading to net photoconversion. Two redox systems have been developed that exhibit apparent electron exchange between components bound at the opposite interfaces. With DHP-bound viologens, kinetic studies have provided evidence that binding is heterogeneous and that transmembrane redox may occur only from certain buried sites. Structural characterization by several techniques is currently under way. Chemical characterization of new dimeric ruthenium μ-oxo ions containing EDTA or 5,5′-carboxy disubstituted bipyridine ligands has been initiated. These studies are prompted by observations that the dimers are capable of catalyzing water oxidation in the presence of suitable strong oxidants. With the EDTA-containing dimer, intermediate oxidation states accumulate during catalyzed oxidation of water by permanganate ion, affording a unique opportunity to study reaction mechanisms.

Pennsylvania State University
University Park, Pennsylvania 16802

177. The Gaseous Free-Radical and Ion Chemistry of Silanes, Germanes, and Phosphines

F.W. Lampe **$160,000**
Department of Chemistry **(24 mo.)**

This research project consists of experimental studies of the chemical reactions initiated by the irradiation of gaseous silanes and germanes with electrons, infrared laser radiation, and vacuum-ultraviolet light. From the experimental studies, fundamental reaction mechanisms relative to this new and unexplored chemistry are developed. In particular, the understanding developed enables us to attempt useful exploitations of photochemical and radiation chemical techniques for the synthesis of amorphous solids of silicon, germanium, and mixtures thereof. Presently under study are the infrared laser photochemistry of SiH_4–D_2, SiH_4–GeH_4, and SiH_4–CH_3Cl mixtures; the vacuum-ultraviolet photochemistry of GeH_4 and SiH_4–GeH_4–NO mixtures; and the ion chemistry of SiH_4–C_2H_6, SiH_4–CH_3Cl, SiH_4–CH_2Cl_2, SiH_4–$CHCl_3$, and SiH_4–CCl_4.

Princeton University
Princeton, New Jersey 08544

178. Surface Chemistry at the Semiconductor–Electrolyte Interface
A.B. Bocarsly **$75,000**
Department of Chemistry

This study encompasses the role of surface chemistry in photodecomposition processes occurring at the II–VI semiconductor–electrolyte interface. Both anodic and cathodic decomposition channels in n-cadmium chalcogenide-based systems are of interest. Recent work has focused on the surface chemistry of n-CdS and n-CdSe photoelectrodes in a $Fe(CN)_6^{4-/3-}$ electrolyte. Illumination of such interfaces produces a layer of $[Cd^{II}Fe^{III}(CN)_6]^-$ on the electrode surface. This overlayer has a zeolitic structure and ion exchange properties that allow the facile transport of alkali cations. Iron sites in this layer are electroactive ($Fe^{II/III}$) and support mediated charge transfer from the semiconductor to solution $Fe(CN)_6^{4-/3-}$. This process is intimately coupled to the flow of supporting cations through the surface layer. The nature of the intercalated cation strongly affects the energy distribution of redox states in the surface layer. Thus, the semiconductor/overlayer interfacial energetics (and kinetics) can be maximized by appropriate choice of the alkali cation. In the case of n-CdS/$Fe(CN)_6^{4-/3-}$ cells, this is accomplished by the addition of a mixture of Cs^+ and K^+. Such cells not only show dramatically improved stability, but yield monochromatic optical-energy conversion efficiencies (488 nm) in excess of 20% with fill factors of ~ 65%. This represents a threefold improvement over previously reported n-CdS-based photoelectrochemical cells. For n-CdSe-based cells, Na^+ ions are found to maximize the overlayer effects leading to energy conversion efficiencies at 633 nm in excess of 40%.

179. Metalloporphyrins as Energy Transfer Catalysts
T.G. Spiro **$104,000**
Department of Chemistry

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

University of Rochester
Rochester, New York 14627

180. Picosecond Studies of Charge Transfer at Semiconductor Liquid Junctions
R.J.D. Miller **$85,000**
Department of Chemistry

The primary objective of this research is to understand the processes associated with interfacial electron transfer. In terms of solar energy conversion, a detailed understanding of the mechanism of surface-mediated electron transfer may enable the prevention of thermal dissipation processes in the solar energy transduction step and thus enable much higher conversion efficiencies. We have developed a new optical method of studying the ultrafast dynamics of surface-mediated electron transfer. We have demonstrated that holographically written diffraction gratings on surfaces are extremely sensitive probes of interfacial dynamics. The first system investigated with this technique was the n-TiO_2/H_2O solar cell. In controlled experiments, the most important finding is that the intrinsic surface-state trapping rates are on the order of 200 picoseconds. Because this is the only competing process for electron transfer, this measurement and quantum yield data placed an upper limit to surface electron transfer rates in this system at 10^{10} sec^{-1}. This rate is not fast enough to compete with vibrational relaxation processes or energy loss mechanisms through heating. Future work will focus on direct measurements of the electron transfer process at surfaces with greater potential for tunneling mechanisms.

181. Applications of Photoinduced Electron Transfer and Hydrogen Abstraction Processes to Chemical and Electrochemical Conversion Processes
D.G. Whitten **$105,800**
Department of Chemistry

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

Stanford University
Stanford, California 94305

182. Energy Transfer Processes in Solar Energy Conversion

M.D. Fayer **$119,000**
Department of Chemistry

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

183. Fundamental Electron Transfer Processes at the Single Crystal Semiconductor/Liquid Interface

N.S. Lewis **$115,000**
Department of Chemistry

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

Syracuse University
Syracuse, New York 13244-1200

184. Photochemical Solar Energy Conversion Utilizing Semiconductors Localized in Membrane Mimetic Systems

J.H. Fendler **$90,100**
Department of Chemistry

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

University of Tennessee
Knoxville, Tennessee 37996-1600

185. Studies of Radiation-Produced Radicals and Radical Ions

T.F. Williams **$108,000**
Department of Chemistry

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

University of Texas
Austin, Texas 78712

186. Organic Redox Phototransformations at Chemically Modified Surfaces

M.A. Fox **$85,000**
Department of Chemistry

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

187. Studies of Photochemically and Electrochemically Driven Electron Transport in Zeolites

T.E. Mallouk **$75,800**
Department of Chemistry

This project involves the preparation of hybrid molecular–solid-state microstructures in which the solid-state component is a zeolite. The zeolite is used as a template for self-assembling chains of photoactive and electroactive molecules. We have prepared assemblies in which small cations (viologens or cationic metallocenes) are exchanged into the bulk of zeolites Y or L, and larger cations (metal polypyridyl complexes or porphyrins) are exchanged onto the outer surface. The vectorial nature of electron transfer in these simple systems is being studied by electrochemistry and by flash photolysis/transient absorbance techniques. With zeolites that are platinized internally, it should be possible to evolve hydrogen from water by using electrochemically reversible electron donors. We are studying electron-transfer quenching of zeolite-surface-bound sensitizers by anionic solution-phase donors. We have prepared linked sensitizer–acceptor (porphyrin–viologen and $Ru(bpy)_3$–viologen) cations. We are now studying the effects of their immobilization on zeolite surfaces on intramolecular electron-transfer rates.

188. Photoinduced Charge Separation by Polymer-Bound Chromophores

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

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

University of California
Berkeley, California 94720

189. Theoretical Studies of Electron Transfer in Complex Media

D. Chandler **$93,600**

This research is concerned with the structure and dynamics of electron-transfer systems in condensed environments, primarily the liquid phase. Current focus is on a model of the $Fe^{2+} \leftrightarrow Fe^{3+}$ exchange in water. Interparticle potentials and pseudopotentials have been constructed that allow us to visualize this system in terms of several hundred H_2O molecules, two Fe^{3+} ions, and a quantal e^- particle. By using quantum Monte Carlo methods, we have discovered an important sampling scheme that allows us to provoke the system to its transition state and therby examine the solvation structures that characterize this state. We are determining the free energy and therefore the probability to attain this state; we also are developing analytical theory to interpret our simulations and real experiments. The next stage of this research will study the role of solvent dynamics in altering the directions of charge transfer. Both classical and quantal aspects of these dynamics (e.g., the role of nonadiabatic transitions) are important. Along with analytical treatments, this work involves the development of methods for performing time-dependent quantum Monte Carlo calculations.

Washington State University
Pullman, Washington 99164-4630

190. Investigations of Charge-Separation Processes in Metal Complexes

G.A. Crosby **$77,000**
Department of Chemistry **(8 mo.)**

This project, which involves charge separation induced by light absorption, explores potential new photosensitizers for solar photochemical energy conversion. The excited-state properties of coordination complexes of Zn(II), Cd(II), and Cu(I) are studied by luminescence spectroscopy in crystalline solids and low-temperature glasses. Preliminary luminescence measurements at low (4 to 77 K) temperatures reveal the existence of energy barriers separating excited $\pi\pi^*$ and ligand–ligand charge-transfer configurations (LLCT). Measurements of decay times and spectra as a function of temperature have been initiated to determine the barrier parameters. Variations of the relative intensities of the $\pi\pi^*$ and LLCT emission bands as a function of excitation wavelength are also under investigation, to optimize the conditions of measuring the singlet–triplet splitting of the LLCT configurations.

Washington University
St. Louis, Missouri 63130

191. Reaction Studies of Hot Silicon, Germanium, and Carbon Atoms
P.P. Gaspar **$81,600**
Department of Chemistry

The project goal is to determine: (1) the reactions of high-energy silicon, germanium, and carbon atoms; (2) how their reactions take place; and (3) how the reaction pathways are influenced by the energy and the electronic states of the free atoms and of the reactive intermediates that they produce. Silicon, germanium, and carbon atoms are formed at high energies by nuclear transformations such as $^{31}P(n,p)^{31}Si$, $^{76}Ge(n,p)^{75}Ge$, and $^{12}C(p,pn)^{11}C$, and at low energies by thermal evaporation of the pure elements. Strong evidence has been found in the past year for the participation of ionic processes in the bond-forming reactions of high-energy silicon atoms recoiling from the $^{31}P(n,p)^{31}Si$ transformation. Methyl group abstraction from tetramethylsilane has been demonstrated for recoiling silicon atoms. This process is unknown for neutral silicon atoms but demonstrated by Lampe for silicon ions. Thermally evaporated germanium atoms have been shown to add to 1,3-butadiene, yielding spiro[4.4]-5-germa-2,7-nonadiene. High-energy carbon atoms recoiling from $^{12}C(p,pn)^{11}C$ have been shown to attack toluene to form benzocyclobutene exclusively by attack on aromatic carbon–hydrogen bonds, but attack on the pi-electron system occurs for the more electron-rich substrate methoxybenzene.

Wayne State University
Detroit, Michigan 48202

192. Dynamics of Charge-Transfer Excited States Relevant to Photochemical Energy Conversion
E.C. Lim **$85,000**
Department of Chemistry

This research addresses basic questions concerning the energetics and dynamics of charge-transfer (CT) excited states that are relevant to photochemical energy conversion. We study CT excited states of electron donor–acceptor (EDA) complexes and transition metal complexes in gas phase and in condensed phase, using laser-based techniques (fluorescence, multiphoton ionization, and so forth). A systematic study of the photophysical properties of EDA complexes containing alkyl benzenes as electron donors reveals that charge recombination is less efficient for D_2A (of sequence DDA) than for DA. Deuteration of methyl hydrogens has relatively large effects on the nonradiative decay rate (k_{nr}) of DA, but only minor effects of k_{nr} or D_2A. The effect of ring deuteration is larger for D_2A than for DA. Results are consistent with the charge delocalization in D_2, which facilitates the charge separation and decreases the magnitude of methyl hyperconjugation. Time-resolved fluorescence indicates that the conformation of DA in the CT excited state is different from that in the ground electronic state, and that the energetics and dynamics of the electronically excited EDA complex can be intrinsically different from those of the corresponding exciplex. The propensity rule for the intersystem crossing of DA and the strong temperature dependence of k_{nr} have been further substantiated. Experiments are presently under way to obtain high-resolution electronic spectra from ultracold gaseous molecules in a supersonic free jet and site-selected molecules in low-temperature matrices.

Chemical Physics

Aerodyne Research, Inc.
Billerica, Massachusetts 01821

193. A Study of CH Reactions Relevant to Combustion-Gasification Processes
S.M. Anderson **$70,000**
Center for Chemical and Environmental Physics

Little is known about carbyne radical reactions, yet these species play an important role in combustion and gasification systems. They also appear to serve as a test bed for studying four-center reactions. The objective of our research is to measure rate coefficients and product channels for CH radicals reacting with other small molecules such as O_2, N_2, NO, and H_2 over a wide temperature range. These studies are conducted using a high-temperature fast-flow reactor, which may be operated up to 1,500 K. CH radicals are produced using atomic sodium to successively abstract bromine atoms from bromoform ($3Na + CHBr_3 \rightarrow 3NaBr + CH$), and detected by laser-excited fluorescence near 430 nm. Results to date include rate constants for the reactions of CH with Cl_2, CH_4, N_2O, O_2, and H_2 at 2 torr and 290 K, which are 15 ± 4, 5.4 ± 1.0, 4.2 ± 0.7, 2.3 ± 0.5, and 0.063 ± 0.012, respectively, in units of 10^{-11} cm^3sec^{-1}. Agreement with other work is satisfactory. Preliminary data for CH + D_2, NO, and N_2 give rate constants of $\sim 7 \times 10^{-11}$, 1.7×10^{-10} (cm^3sec^{-1}), and 1.2×10^{-31} (cm^6sec^{-1}). Extension of this work to other molecules and higher temperatures is under way.

Aerospace Corporation
Los Angeles, California 90009

194. A Shock Tube Study of the Reactions of Hydroxl Radicals in the Combustion Species
J. Bott, N. Cohen **$72,000**

The project objective is to use shock tube techniques to measure the rate coefficients for OH reactions important for understanding and predicting hydrocarbon combustion. The experiments will be performed at combustion temperatures of 1,200 K and higher and at near-atmospheric pressure. Reaction partners to be studied will include ethylene, propylene, acetylene, formaldehyde, acetaldehyde, methanol, ethanol, acetone, and iso-octane. Transition state theory calculations will be used to relate the measurements to other data at lower temperatures so that reliable temperature dependences of the rate coefficients under study (and those of analogous reactions) can be established.

University of Arizona
Tucson, Arizona 85721

195. Chemical Activation of Molecules by Metals: Experimental Studies of Electron Distribution and Bonding

D.L. Lichtenberger **$84,000**
Department of Chemistry

This project is directed toward providing an experimental basis for the electronic structure factors that control the stability and reactivity of organic molecules and fragments bound to metals. The primary spectroscopic techniques are valence (HeI, HeII, UPS), core (XPS), and Auger spectroscopy of both gas-phase organometallic molecules and surface species. New capabilities have been accomplished in the UPS of organometallic thin films, and improved instrumentation is being developed for gas-phase XPS and Auger spectroscopy. The systematic study of electron-poor to electron-rich metals with carbonyls, hydrides, alkyls, alkylidenes, alkylidynes, alkoxides, and a variety of π-bonded organic molecules is providing a more complete experimental foundation for the electron distribution and bonding in these species. As a specific example, a comparison has been made of the electronic factors in activation of alkenes and alkynes by electron-rich and electron-poor metals. The electron-poor metals are dominated by metallocyclopropene character that favors addition (polymerization) reactions. The electronic structure factors in different stages of C–H bond activation have also been established with experiments on metal–olefin–hydrides and on an organometallic molecule that displays a three-center M–H–C interaction. The ionization energies are directly related to the thermodynamics of the chemical processes.

Arizona State University
Tempe, Arizona 85287

196. Electronic Structure and Reactivities of Clusters Containing Very Heavy Atoms

K. Balasubramanian **$75,000**
Department of Chemistry

We are currently investigating the electronic structure and reactivities of heavy main group and transition metal clusters. Such clusters are useful models of surfaces, and the study of their reactivities and structural properties can provide a wealth of information on catalysis and chemisorption. Reactivities and other properties of those clusters show dramatic size dependence. Particular clusters of current interest are main group clusters (Ga_xAs_y, Sn_x, Ge_x, Ga_x) and transition metal clusters (Au_x, Ag_x, Y_x, Pt_x, Pd_x, and so forth). The properties investigated are geometries, ionization potentials, spectroscopic properties (R_e, T_e, ω_e for smaller clusters), separation of low-lying excited states, and so forth. Reactivities of these clusters are also investigated with model reactions. We are currently investigating the $M + H_2$ reactions for a number of metals M. Electronic structures of MH (M = transition metal) molecules are being investigated to understand the nature of metal–hydrogen bonds. These investigations are conducted using a complete active space MCSCF followed by higher order configuration interaction calculations. Relativistic effective core potentials are used for the heavy atoms in the molecule. Spin-orbit interaction and correlation are introduced simultaneously using a relativistic configuration interaction method.

Brown University
Providence, Rhode Island 02912

197. Interactions of Molecules with Surfaces

E.F. Greene **$78,000**
Department of Chemistry

The energy dependence of the yields of Na^+ ions formed when beams of Na atoms hit a Si(111) surface at a temperature T is that expected for equilibrium for kinetic energies E of the incident atoms lower than 0.72 eV. Above this threshold energy E_{th} the yields are nearly independent of T. They rise abruptly to a maximum of about 0.6 at $E \simeq 3$ eV and then decrease slowly to ~ 0.3 at E = 30 eV. Interpretation of the results suggests that for $E < E_{th}$ the ions are trapped by the surface and then slowly desorbed, mostly as neutral Na, while those with $E > E_{th}$ reflect directly as ions. At the higher energies some penetration of Na to the bulk Si is likely. The value of E_{th} permits an estimate that the electron transfer occurs at about 6 A from the surface in a time tau $\simeq 4 \times 10^{-14}$s for an atom approaching at 2.5 kms^{-1}. The isomerization of perfluoroDewarbenzene (PFDB) to perfluorobenzene (PFB) can be caused by the impact on Teflon surfaces of fast molecules, produced in nozzle beams having PFDB seeded into inert carrier gases: H_2, He, N_2, Ar, and Kr. The largest yields are found with Ar although the speed of the PFDB is lower than with H_2 and He. A possible resolution to this paradox is that the heavier carrier gases are able to heat the surface enough to transfer to the PFDB the activation energy required for its isomerization.

University of California
Davis, California 95616

198. Laser Studies of the Dynamics of Atom–Molecule Reactions

W.M. Jackson **$58,000**
Department of Chemistry

The temperature dependence of the rate constant for the reaction of CN radicals with various organic molecules is being investigated. It has been observed that the rate constant decreases with increases in temperature. This is in agreement with the expectations based upon our previous modeling of the room-temperature rate constants. That model suggests that the reaction is controlled by long-range attractive forces that result in orbiting trajectories around the reactant partner. These orbiting collisions enhance the possibility for the reaction during the encounter. Preliminary studies have begun on the use of a transient infrared spectrometer to monitor gas-phase reactions induced by laser photolysis of free-radical precursors. These experiments couple fast detectors and a modified Perkin-Elmer model 180 spectrophotometer with a computer-controlled transient digitizer, to integrate transient infrared absorption signals. The first series of experiments will investigate room-temperature reactions of methyl radicals.

University of California
Irvine, California 92717

199. Laser Studies on Internal State Dependence of Excitation and Deexcitation Processes
E.K.C. Lee, J.J. Valentini **$67,640**
Department of Chemistry

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

California Institute of Technology
Pasadena, California 91125

200. Studies in Spectroscopy and Chemical Dynamics
A. Kuppermann **$89,100**
Chemistry and Chemical Engineering Division

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

Catholic University of America
Washington, District of Columbia 20064

201. Kinetics and Mechanisms of Key Elementary Processes of Importance to High-Temperature Combustion Chemistry
M.C. Lin, W.A. Sanders **$69,230**
Department of Chemistry

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

University of Chicago
Chicago, Illinois 60637

202. Quantum Dynamics of Fast Chemical Reactions
J.C. Light **$77,000**
James Franck Institute

This project will combine three theoretical innovations that will provide an efficient and accurate means of determining thermal (or detailed) rate constants for fast gas-phase reactions. The following innovations have been used separately on model systems: (1) formulation of the thermal rate constant as the time integral of trace of the flux–flux autocorrelation function evaluated on an arbitrary surface dividing reactants and products; (2) use of a distributed local (Gaussian) basis representation of the flux operators to reduce the number of nonzero vectors; and (3) quantum time propagation of the nonzero vectors of the flux operators by a "reduced Lanczos propagation technique." The combination of these techniques should make feasible the accurate quantum evaluation of rate constants for fast- and few-atom systems.

University of Colorado
Boulder, Colorado 80309-0215

203. Laser Photoelectron Spectroscopy of Ions
G.B. Ellison **$95,000**
Department of Chemistry

This project involves the spectroscopic study of ions and radicals likely to be reactive intermediates in combustion processes. We prepare mass-selected ion beams and cross them with the output of a CW ArII laser operating on a single line (λ_0 = 488 nm). The laser detaches electrons from the negative ions (M^-) and we use a set of hemispherical analyzers to monitor the kinetic energy (KE) of these scattered electrons, $M^- + \hbar\omega_0 \rightarrow M + e^-(KE)$. We have studied a variety of carbanions such as the methide ions ($^-CH_2NC$ and CH_2CN^-), the acetyl anion ($CH_3\text{–}CO^-$), and the vinyl ion ($CH_2\text{–}CH^-$). For example, studies of the CH_2CN^- ion furnish the following electron affinities: $EA(CH_2CN) = 1.543 \pm 0.014$ eV and $EA(CD_2CN) = 1.538 \pm 0.012$ eV. From analyzing the peak splittings and intensities, we extract potential energy curves for the umbrella mode of the CH_2CN^- negative ion and the CH_2CN radical. Using the gas-phase acidity of CH_3CN, we obtain the following bond dissociation energy for acetonitrile: $DH^0{}_{298}(H\text{–}CH_2CN) = 94.2 \pm 2.0$ kcal/mol. The isomeric ion, $^-CH_2NC$, has also been scrutinized. We find $EA(CH_2NC) = 1.059 \pm 0.024$ eV and $EA(CD_2NC) = 1.070 \pm 0.024$ eV. Isocyanomethide is a pyramidal species and a localized ion. Using our EA value and the gas-phase acidity, we find the following bond dissociation energy: $DH^0{}_{298}(H\text{–}CH_2NC) = 84.8 \pm 3.1$ kcal/mol.

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

S.R. Leone **$85,000**
Department of Chemistry and Biochemistry

This research involves (1) the generation of various free radicals by selective photolysis mechanisms and (2) the study of the reactivity and energy transfer of these radicals with other species. These studies are carried out by excimer laser photolysis and time- and wavelength-resolved, low-resolution infrared emission. We have adapted a Fourier transform infrared spectrometer (FTIR) for use in time-resolved emission, to probe high-resolution features of these radical species and their subsequent reactions. Recent results include: (1) absolute rate coefficients for the reaction of CD_3 with HBr and HI, (2) a detailed study of the photofragmentation infrared emission from the CO and CH_3 fragments in acetone photolysis, (3) the first results on time-resolved infrared emission of photofragments taken with an FTIR (applied to chloroethylene molecules), and (4) a series of measurements on the vibrational deactivation rates of the methyl radical antisymmetric stretch.

Columbia University

New York, New York 10027

205. *Energy Partitioning in Elementary Gas-Phase Reactions*

R. Bersohn **$75,000**
Department of Chemistry

Elementary atom–molecule reactions are studied by laser-induced fluorescence, and spectroscopic techniques for detection of atoms are developed. Hydrogen (H) atoms are detected immediately after their production by chemical reactions or photodissociation. Use of a narrow-band laser permits the determination of the Doppler broadened line shape of the 1s → 2p absorption that yields the velocity distribution. The cross sections and translational energy release in hydrogen–deuterium exchange reactions caused by collision of fast H atoms with deuterium-containing molecules are being measured. A study has been completed of the cross section versus energy for H atoms reacting with deuterium molecules. Results are being obtained for collisions of H atoms with deuterated or partially deuterated methane, acetylene, and ethylene. Hydrogen atoms are being generated from a series of methyl-containing benzenes and ethylenes, to which fixed amounts of energy have been added by light absorption. The measured rates of evolution of the H atoms and their kinetic energies constitute a crucial test of unimolecular reaction rate theory.

Cornell University

Ithaca, New York 14853

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

T.A. Cool **$80,000**
Department of Applied and Engineering Physics

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

Emory University

Atlanta, Georgia 30322

207. *Theoretical Studies of Combustion Dynamics*

J.M. Bowman **$71,360**
Department of Chemistry

The objective of our current research is to establish a quantum mechanical theory of recombination reactions and to apply it to a study of the H + CO → HCO reaction, an important process in hydrocarbon combustion. We have achieved the first objective by generalizing a theory of atom–atom recombination due to Smith. The key quantity is the time delay due to the collision. The calculation of this quantity for the H + CO system is proceeding with large-scale coupled channel scattering calculations being performed on the MFE CRAY-XMP supercomputer. An accurate *ab initio* potential, due to Harding, is being used in these calculations. Thus far we have obtained the time delays over a wide range of energies for the simplest case of zero total angular momentum and treating CO as rigid rotor and as vibrating rotor. We have also obtained the branching probabilities for the HCO collision complex as it decays into all final rotational states of CO for all possible initial rotational states. These benchmark calculations will be used to test various approximate theories. In particular we intend to test the RRKM theory immediately after our calculations are complete. When complete, these calculations will provide the most accurate predictions of the rate of recombination of H with CO.

Howard University

Washington, District of Columbia 20059

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

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

This project includes the study of kinetics and fluorescence spectra of alkoxy radicals RO ($R=CH_3O$, C_2H_5O, $i\text{-}C_3H_7O$, and $t\text{-}C_4H_9O$), which are important species in the combustion of hydrocarbons. The RO radicals are produced from the laser photolysis of RONO at 355 nm, and the reaction rates of RO with NO, NO_2, and O_2 are obtained by following the time-dependent decreases of intensity of laser-excited fluorescence of RO at 337 nm. The rate constant of NO with i-C_3H_7O is about 10^{-11}; and with O_2 is $< 10^{-14}$ in $cm^3 molec^{-1} s^{-1}$. The fluorescence lifetime of i-$C_3H_7O^*$ produced at 193 nm photolysis is 0.87 microsecond, which is somewhat shorter than those of CH_3O and C_2H_5O. Further study involves laser photolysis combined with flash absorption spectroscopy and ESR detection to measure kinetics of polyatomic radicals and triplets in acetylenic systems; and measurements of the threshold energy of CH_3O^* dissociated from CH_3OCH_3 photolysis. The threshold energy corresponds to the sum of the C–O bond dissociation energy and electronic energy of CH_3O^*.

University of Illinois
Chicago, Illinois 60680

209. *Kinetics of Elementary Atom and Radical Reactions*
R.J. Gordon **$80,000**
Department of Chemistry

The objectives of this research are to measure the reaction rates and to study the dynamics of elementary gas-phase reactions. We have studied the importance of tunneling in the reaction of ground-state oxygen atoms with HD. The branching ratio for this reaction was determined using laser-induced fluorescence to measure the relative concentrations of OH and OD products. We discovered that the reaction mechanism is dominated by tunneling below 450 K. In a second study the relaxation of highly excited molecules has been investigated using a CO_2 laser to excite a donor molecule while detecting infrared fluorescence from an acceptor molecule. For $SF_6 + N_2O$ we measured the rate of vibrational energy transfer to N_2O as a function of SF_6 energy. We have found that the bending mode of N_2O is preferentially excited and that it relaxes an order of magnitude more slowly than the asymmetric stretching mode. In a third study we investigated the production of electronically excited triplet NH(A) radicals generated by photolyzing a mixture of HNCO, O_2, and Ar. The mechanism for this phenomenon involves energy pooling by two singlet metastable species, which are most probably NH(b) and O_2(a).

210. *Shock Tube Studies of High-Temperature Hydrocarbon Pyrolysis Kinetics*
J.H. Kiefer **$85,000**
Department of Chemical Engineering

The purpose of this project is to determine rates and mechanisms for fuel hydrocarbon pyrolysis at high temperatures. The measurements are made in a shock tube (providing arbitrary, precise, and externally set temperatures) with two very high resolution laser diagnostic techniques: laser schlieren measurement of density gradient (net endothermic rate) and a new method of excimer laser flash absorption, which provides absorption profiles in the ultraviolet with ~ 0.03 microsecond resolution. Previous work has defined much of the pyrolysis kinetics of propane, propene, ethane, ethylene, benzene, and 1,3-butadiene. Recent measurements have given a mechanism and rate for ethylbenzene decomposition and a partial understanding of toluene pyrolysis. Flash absorption measurements at 220 nm have now confirmed the rate and mechanism for 1,3-butadiene dissociation derived from the laser schlieren data. Recent laser schlieren work has been the study of cyclohexene dissociation to 2,000 K, and a new study of vinyl acetylene pyrolysis. Flash absorption measurements have also been obtained for the cyclohexene dissociation.

Illinois Institute of Technology
Chicago, Illinois 60616

211. *Studies of Combustion Kinetics and Mechanisms*
D. Gutman **$140,000**
Department of Chemistry

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

University of Iowa
Iowa City, Iowa 52242

212. *Determination of Step-Size Parameters for Intermolecular Vibrational Energy Transfer*
D. Tardy **$75,580**
Department of Chemistry

Intermolecular energy transfer of highly excited polyatomic molecules plays an important role in many complex chemical systems, and involves both the excitation process in thermally activating molecules for reaction and the deactivation process in stabilizing activated molecules. Energy transfer is particularly relevant to high-temperature reactions and the feasibility of mode-selective chemistry. Very little fundamental information has been obtained on the important parameters for quantification of energy transfer rates for large polyatomics (more than eight atoms) at levels of excitation corresponding to chemical reaction. The primary objective of this project is to experimentally obtain average energy step sizes for the removal of vibrational energy via bimolecular gas-phase collisions for a homologous series of photoactivated and chemically activated substrates. The step size will be determined as a function of the molecular complexity of the collision partners, excitation energy of the substrate, and attractive interactions between collision partners. We will obtain the average step size by simultaneously monitoring the decay of the infrared emission intensity of at least two vibrational modes of the energized substrate. The partitioning of vibrational energy between relative translation and vibrational energy of the collision partners will also be determined by monitoring the infrared emission of the respective deactivator.

University of Kentucky
Lexington, Kentucky 40506-0055

213. Laser Spectroscopy and Dynamics of Combustion Intermediates

D.J. Clouthier **$53,400**
Department of Chemistry

Experiments are in progress to study the vibrational and electronic spectra and excited-state dynamics of a variety of sulfur-containing species that are analogs of important oxygen-containing combustion intermediates. The visible absorption spectra of S_2O and H_2CCS have been recorded for the first time and analyzed. Supersonic jet-cooled spectroscopy of H_2CS and measurements of SRL lifetimes are in progress. Searches for the electronic spectra of the free radicals HCS and C_2S are also under way. A high-temperature jet has been constructed that will allow us to pyrolyze molecules at temperatures up to 1,000°C in the zone immediately before the nozzle, providing a unique source of transient species.

University of Massachusetts
Amherst, Massachusetts 01003-0035

214. Theory of the Dissociation Dynamics of Small Molecules on Metal Surfaces: Finite Temperature Studies

B.E. Jackson **$32,180**
Department of Chemistry

A full understanding of catalysis on metals has been hindered by the difficulty of developing reactive molecule–surface scattering theories capable of properly including all important molecular degrees of freedom, as well as the thermal and electronic excitations of the solid. Time-dependent quantum mechanical techniques are being used to address this problem. These methods use discrete representations of the molecular wave function, and can easily accommodate semiclassical approximations when valid. A full six-dimensional model for the dissociative adsorption of a diatomic molecule on a metal has been developed. A computationally efficient method for quantum mechanically extending these calculations to include the thermal fluctuations of the surface atoms is also being developed. Dissociative sticking probabilities for a variety of light diatomics will be computed as a function of the kinetic and internal energy of the molecule, and the surface temperature, for several model metal–molecule interactions. These same techniques will be used to study adsorbate mobility on surfaces, hydrogen diffusion in metals, and finite temperature nonreactive molecule–surface scattering.

Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

215. Aromatics Oxidation and Soot Formation in Flames

J.B. Howard **$98,000**
Department of Chemical Engineering

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

216. Spectroscopic and Dynamical Studies of Highly Energized Small Polyatomic Molecules

J.L. Kinsey, R.W. Field **$132,000**
Department of Chemistry

A new technique developed in this laboratory, stimulated emission spectroscopy (SEP), has provided spectra of vibrationally excited acetylene $\tilde{X}\ {}^1\Sigma_g{}^+$ of unprecedented quality and extent. Two energy regions have been explored, one in the neighborhood of ~28,000 cm^{-1} of vibrational excitation and one at ~11,400 to 15,600 cm^{-1} of excitation. The higher energy region showed "clumps" of levels spaced a few cm^{-1} apart, with each clump containing ~50 resolvable levels. These spectra provided the first experimental molecular data that could be examined in relation to theories of chaotic behavior in quantum systems. Statistical tests developed in nuclear physics were applied to the data, and powerful new statistical diagnostics were developed. In the lower energy region an unexpectedly large density of levels was observed, which may be related to acetylene's structural isomer vinylidene (H_2CC). Also, at ~15,600 cm^{-1}, the SEP spectra reveal an ~30 cm^{-1} region of strongly mixed levels. These showed a rotation-dependent signature predicted to appear in the neighborhood of the vinylidene by group theory based on the complete nuclear permutation-inversion group. A sideline study of the electronically excited $\tilde{A}$ state of acetylene revealed a previously unsuspected Fermi resonance, which led to an improved set of vibrational constants for this state. Studies of quantum beats and anticrossing spectroscopy of $\tilde{A}$-state levels in the presence of a magnetic field have led to information about triplet states of acetylene. This work seems on the verge of yielding a new limit on the value of the HCC–H bond strength, which is critical in kinetic modeling of combustion symptoms.

University of Michigan
Ann Arbor, Michigan 48109-2143

217. ***Energy-Transfer Properties and Mechanisms***
J.R. Barker **$83,000**
Department of Atmospheric and Oceanic Science

This project studies the mechanisms and properties of energy transfer involving moderate-sized molecules. By a combination of experiments and theoretical investigations, we hope to gain a fuller understanding of highly vibrationally excited molecules and to develop a workable theoretical model of the energy-transfer process. In part, the experimental investigation focuses on resolving current controversies about the temperature- and energy-dependence of the average energy-transfer step-size. We are obtaining new experimental data with improved techniques, such as time- and wavelength-resolved infrared fluorescence, which are used to monitor the vibrational energy in excited molecules prepared by pulsed laser excitation. In order to investigate the mechanisms of energy transfer, we plan to study isotopically substituted isomers and to determine the effects of dipole moment, symmetry properties, fundamental vibrational frequencies, and so forth. In the theoretical effort, we are developing better models of internal state densities and the infrared emission from highly excited molecules. We are using collision-al/reaction master equation calculations to model our experiments and to investigate the manifestations of energy transfer under extreme conditions. For example, we are investigating whether a more detailed unimolecular rate theory is needed to account for the nonsteady-state conditions that can occur in reactions at extremely high temperatures and moderate pressures.

University of Minnesota
Minneapolis, Minnesota 55455

218. ***State-to-State Dynamics of Molecular Energy Transfer***
W.R. Gentry, C.F. Giese **$97,000**
Departments of Chemistry and Physics

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

219. ***Variational Transition State Theory***
D.G. Truhlar **$80,000**
Department of Chemistry

This project is concerned with the application of variational transition state theory and semiclassical tunneling calculations to gas- and solution-phase reactions. Recent progress includes: (1) applications to atom–diatom and polyatomic reactions using global or semiglobal analytic representations of potential energy surfaces and the development and testing of such representations; (2) development of new methods for combining *ab initio* electronic structure calculations of reaction-path potentials with variational transition state theory and semiclassical reaction-path tunneling calculations; (3) development of a new, general-purpose computer code for calculations on polyatomics; and (4) study of the effect of vibrational excitation on chemical reaction rates.

National Bureau of Standards
Gaithersburg, Maryland 20899

220. ***Laser Studies of Chemical Dynamics at the Gas–Solid Interface***
R.R. Cavanagh, D.S. King **$75,000**
Center for Chemical Physics

The project involves experimental measurements of the internal-state and kinetic energy distributions of molecules desorbed from metal surfaces in ultrahigh vacuum, to understand energy transfer at a microscopic level. Molecules are desorbed by resistive heating or by nonresonant laser heating and are probed by laser-excited fluorescence techniques. Statistical energy distributions are always observed following thermal desorption; however, full rotational or translational accommodation is not always obtained, reflecting the operative dynamics. Laser heating of platinum foils with monolayer coverages of nitric oxide produced desorbed NO species with non-Boltzmann velocity distributions, excess vibrational energy, and a nonstatistical spin-orbit distribution. There is no universal relationship between rotational, vibrational, kinetic, or electronic energy distributions of these desorbing species. Experiments are in progress on Pt(111) that will utilize nanosecond and picosecond heating lasers to probe these apparently nonstatistical dynamics.

221. ***Kinetics Data Base for Combustion Modeling***
J.T. Herron **$125,000**
Center for Chemical Physics

The goals of this project are (1) to compile and evaluate data on the chemical kinetics of gas-phase reactions and (2) to provide a consistent set of recommended rate constants for use by modelers, chemical kineticists, and theoreticians. Focus is on the elementary single-step thermal reactions relevant to the combustion of organic compounds. Work has been completed on the evaluation of data on the methane oxidation system, the reactions of oxygen-containing C_2 species, reactions of the C_3 and C_4 hydrocarbons, and the reactions of ground-state oxygen atoms with unsaturated compounds, sulfur-containing species, and saturated compounds. Data have been evaluated on over 750 reactions. A compilation of data on combustion-related reactions of nonaromatic species for the period 1972 to 1982 has been prepared, which provides unevaluated data on 1,980 reactions. Current activities involve further expansion of the combustion data base to include reactions of propene and the isobutyl radical. About 85 reactions are being evaluated. We plan to evaluate data on (1) the reactions of small free radicals, such as H, O, OH, and OH_2; (2) the reactions involved in NO_x formation and destruction; (3) the reactions involving aromatic and heterocyclic species; and (4) the reactions of free radicals with other unsaturated species.

University of New Orleans
New Orleans, Louisiana 70148

222. *Identification and Temporal Behavior of Radical Intermediates Formed During the Combustion and Pyrolysis of Gaseous Fuels*
R.D. Kern, Jr. **$68,900**
Department of Chemistry

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

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

223. *Multiphoton Interactions in Molecules with Picosecond Laser Pulses*
H.-S. Kwok **$70,500**
Department of Electrical and Computer Engineering

High-power picosecond laser pulses are employed in this project to study the absorption spectra of vibrationally excited polyatomic molecules. Tunable 20 to 200 ps CO_2 and dye laser pulses are used in a pump-probe arrangement to measure the excitation characteristics of vibrationally hot molecules. Intramolecular and intermolecular energy transfer rates are studied in the collisional and collisionless regimes. Information on the vibrationally hot molecules in the quasi-continuum is of vital importance in the understanding of gas-phase reaction dynamics. During the past year, it was found that the absorption spectra of excited molecules, such as C_2F_5Cl and SF_6, are pulse-duration dependent. At very low probe pulse intensities, the vibrational absorption spectra are clean Lorentzians with zero background. As the duration increases, the spectra evolve into broad structures with nonzero background for all frequencies. Such behavior was observed for the first time and provided information on the intramolecular transfer of energy. We also have obtained preliminary results on ultraviolet–infrared double resonance spectroscopy of CrO_2Cl_2. The technique of nonresonant multiphoton ionization can be used to probe the transfer of energy in the electronic excited state.

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

224. *Multiphoton Ionization Spectroscopy and Photochemistry of Transient Species*
P.M. Johnson **$73,630**
Department of Chemistry

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

University of Oregon
Eugene, Oregon 97403-0237

225. *Reactive Collisions of High-Temperature Systems*
M.M. Graff **$82,660**
Chemical Physics Institute

A neutral beam apparatus is being developed to study reactive collisions of neutral systems whose endothermicities or activation barriers preclude study by molecular beam techniques. This project will investigate the dependence of reactivity on collision energy and on molecular internal energy. Systems under study include the basic oxygen–hydrogen reactions $O + H_2 \rightarrow OH + H$ and $OH + H_2 \rightarrow H_2O + H$. The project is based on a double mass spectrometer design, modified for the study of neutral species. Production of a velocity- and mass-selected beam of radicals will be effected by photodetachment within the extended cavity of an argon ion laser. The dependence of reactivity on H_2 rotational energy will be studied by use of a temperature-controlled reaction cell. The structure of the excitation function will be observed for the entire range of chemically interesting collision energies (threshold-several eV).

University of Pennsylvania
Philadelphia, Pennsylvania 19104

226. *Dynamics of Vibrationally Excited Polyatomic Molecules and Their Unstable Isomers on the Electronic Ground State Potential Surface*
H.-L. Dai **$98,000**
Department of Chemistry

This project will generate crucial information for the understanding and design of chemical reactions of highly vibrationally excited molecules. Experiments will reveal the fine details of structure and dynamics on the electronic ground state for many chemical species important in the chemistry of energy production. One of our endeavors is to identify the transient isomers existing at high vibrational energies of the electronic ground state. The approach is to first prepare a large population of excited molecules in a selected, single vibrational level, using the method of stimulated emission pumping (SEP), and then to detect the infrared emission from the prepared level. The frequency-resolved infrared fluorescence spectra can be used to elucidate intramolecular vibrational dynamics and isomerization reactions. The vinylidene isomer on the acetylene potential surface will be studied. A novel spectroscopic method for high vibrational levels, stimulated emission polarization spectroscopy, has been developed in our laboratory. Currently we are applying this technique on the methylene radical. The high vibrational levels of radicals are very difficult to study and very little is known about vibrationally excited radicals. SEP will allow the preparation of large quantities of radicals selectively excited in a high vibrational level. Chemical reactions of vibrationally excited radicals can thus be studied.

227. *Half-Collision Studies of Inelastic Energy Transfer Processes*

M. Lester **$98,000**
Department of Chemistry

The project objective is to investigate half-collision analogs of vibrational and rotational relaxation processes. State-to-state studies of the photofragmentation dynamics of hydroxyl–rare-gas (OH–RG) van der Waals (vdW) complexes provide details of the exit channel of an inelastic energy-transfer step. Initial vibrational and/or rotational excitation localized in the OH moiety is transferred to vdW vibrational motions, resulting in rupture of the weak OH–Rg bond. Spectroscopic examination of the OH photofragments probes the nascent internal product state distribution. The determination of excess energy in product translation, vibration, rotation, and electronic degrees of freedom provides information on various relaxation channels. The nascent OH rotational distribution is expected to reveal the exit channel interaction potential between the recoiling OH and rare gas atom. Time evolution of the dissociation event is measured directly by double resonance methods or indirectly by spectral line broadening of vdW excitation features.

University of Pittsburgh
Pittsburgh, Pennsylvania 15260

228. *High-Resolution Infrared Spectroscopy: Dynamics of Vibrational Excited States*

K. Janda **$33,000**
Department of Chemistry

Recent pump-probe results have provided state-to-state dynamics information for the vibrational predissociation reactions of the type $HeCl_2$ (v,j,k) $\rightarrow$ He + Cl_2 (v′,j′). Complete analysis of such data requires precise spectroscopic data for the "half collision" complex $HeCl_2$. The project objective is to provide such data for helium, neon, or argon bonded to Cl_2 or Br_2. We believe that detailed study of these simple molecules will lead to general principles useful in understanding the molecular dynamics of combustion reactions.

Princeton University
Princeton, New Jersey 08544

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

F.L. Dryer **$95,110**
Department of Mechanical and Aerospace Engineering

This project is an integrated effort to determine the reaction mechanisms responsible for oxidation of hydrocarbon and oxygenated hydrocarbon molecular structures under conditions representative of combustion environments. Such mechanisms are useful for identifying areas where further elementary processes research would be most beneficial, in acting as benchmarks against which simplified empirical chemistry results can be compared, and in evaluating the interactions of combustion chemistry within simple one-dimensional, time-transient systems with transport. The approach consists of (1) experimental determination of pyrolysis and oxidation intermediate and product profiles in a turbulent flow reactor; (2) comprehensive mechanism development and accompanying computer modeling; and (3) application of newly available sensitivity analysis computer tools to extract the maximum information from the first two parts of the research. Efforts are coordinated with sensitivity analysis research at Princeton, modeling efforts at Lawrence Livermore National Laboratory, and a fundamental kinetics program at Brookhaven National Laboratory. The experimental aspects of the project are conducted in a flow reactor facility developed at Princeton that permits chemical kinetic observations at atmospheric pressure, in the temperature range of about 900 to 1,200 K, and for reaction times on the order of 10 to 500 ms. The modeling aspects of the project are accomplished through use of several recently available computational tools (e.g., HCT, AIM, and CHEMSEN) and other tools and techniques as they become available. Chemical systems of current interest (in order of increasing complexity) are: the addition of small amounts of hydrocarbons to the $CO–H_2–O_2$ system, the formaldehyde pyrolysis and oxidation systems, the acetaldehyde pyrolysis and oxidation systems, and the pyrolysis and oxidation systems of simple alcohols and other oxygenated hydrocarbons.

230. *Aromatic-Radical Oxidation Kinetics*

I. Glassman, K. Brezinsky **$76,980**
Department of Mechanical and Aerospace Engineering

The realization that aromatics would be a major constituent in alternative fuels with significant attendant consequences on soot formation and fuel stability has provided a recent practical impetus for detailed studies of the combustion chemistry of these species. Such detailed understanding is necessary for combustor modelers and to assist in unraveling reasons for the great sooting tendency of aromatic compounds. We are initiating a series of atmospheric-pressure turbulent-flow-reactor experiments to elucidate the importance of oxygen atom addition to the aromatic ring and the displacement of a hydrogen from the ring during the high-temperature (1,100 K) oxidation of benzene and toluene. NO_2, which, in a set of preliminary experiments, dramatically alters the oxygen atom concentration during oxidation experiments, will be used in a systematic manner to perturb the radical pool concentrations and to influence intermediate species production. The judicious use of the additives NO, N_2O, and $(CH_3)_2CN(OH)$ during the oxidation studies will amplify the experimental results of the NO_2 studies. Phenol, a possible product of oxygen atom addition or hydrogen displacement by OH, has been the object of pyrolysis experiments. Using the flow reactor data and a steady-state analysis, a mechanism for the pyrolytic degradation of phenol has been developed that will aid in understanding future oxidation experiments.

231. *Dynamical Studies of Molecular Systems*
H.A. Rabitz **$128,980**
Department of Chemistry

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

Purdue University
West Lafayette, Indiana 47907

232. *Measurement of Species Concentrations in Flames by Laser-Induced Fluorescence*
N.M. Laurendeau **$87,000**
Department of Mechanical Engineering **(18 mo.)**

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

Rensselaer Polytechnic Institute
Troy, New York 12180-3590

233. *Kinetic Measurements on Elementary Fossil Fuel Combustion Reactions over Wide Temperature Ranges*
A. Fontijn **$73,000**
Department of Chemical Engineering

This project provides kinetic data on important combustion reactions between atoms and molecules, by using the high-temperature photochemistry (HTP) technique. This technique allows measurements to be made on such reactions in isolation in the 300 to 1,800 K range in a single reactor, which provides an essentially wall-less reaction region. We have completed studies of the reactions of O atoms with ethylene, acetylene, H_2, and D_2, and are working on those with ethane and 1,3-butadiene. In all but one case ($O + H_2$) the measurements above 1,000 K are the first by a direct technique, and in all cases they give the first comparison in one apparatus between low ($<$ 1,000 K) data and those obtained in high-temperature multireaction media, such as flames and shock tubes. Agreement with other direct low-temperature measurements is good. The agreement with flame data is poor, as expected from results in those multireaction media. Agreement with shock tube data in the 1,500 to 2,500 K range is good for C_2H_2, H_2, and D_2, but poor for C_2H_4 due to uncertainties in the assumptions on secondary reactions in the shock tube. The k(T) values obtained for H_2 and D_2 compare well with *ab initio* calculations; the results have allowed good estimates of quantum-mechanical tunneling contributions.

Rice University
Houston, Texas 77251

234. *Infrared Absorption Spectroscopy and Chemical Kinetics of Free Radicals*
R.F. Curl, Jr., G.P. Glass **$70,000**
Department of Chemistry

This research is directed at the detection, monitoring, and study of the chemical kinetic behavior of small free-radical species (thought to be important intermediates in combustion) by infrared laser absorption spectroscopy. The kinetics and mechanisms of several reactions of free radicals in combustion are being investigated using free radicals and atoms produced by excimer laser flash photolysis and monitored by infrared absorption spectroscopy. The rate constants of the reactions of C_2H with acetylene and with O_2, H_2, HCCH, and NO have been measured. In future work, the reactions of O atoms (^3P and ^1D) with acetylene and ethylene will be investigated. The infrared electronic spectrum of C_2H and C_2D is being investigated. The six bands of C_2H and the three bands of C_2D that we have analyzed arise from vibronic coupling between the ground and excited electronic states. Recently, the cause of this enormous coupling has been suggested by the *ab initio* calculations of Kraemer, which predict that the potential surfaces of this molecule undergo a cusp crossing in the linear geometry near the minimum energy geometry of the excited state. Based on the *ab initio* work and experimental study of ^{13}C isotopes, the vibronic coupling in this molecule may be analyzed. Plans for future spectroscopic studies include HCCN, CH_2OH, CH_3O, and N_2H_3.

235. Supersonic Bare Metal Cluster Beams
R.E. Smalley **$85,000**
Department of Chemistry

Our recent advances in the generation of cold negative cluster ion beams of transition metals have enabled two key measurements to be made of the electronic structure of such clusters. The first is the direct measurement of the adiabatic electron affinity (EA) of the metal cluster by laser detachment of the cold negative cluster ion. The adiabatic EA is measured on the lowest photon energy that detaches the extra electron in a one-photon process. The second key measure of electronic structure is the ultraviolet photoelectron spectra (UPS) of the metal cluster. A novel and quite general technique has been developed for the recording of such UPS spectra, involving a pulsed magnetic time-of-flight photoelectron spectrometer. First applications of these vitally important new probes of bare metal cluster electronic structure have now been published.

University of Rochester
Rochester, New York 14627

236. Low-Energy Ion–Molecule Reaction Dynamics and Chemiionization Kinetics
J.M. Farrar **$78,800**
Department of Chemistry

Molecular beam reactive scattering measurements have been performed on a number of chemical systems to correlate reaction dynamics with potential surface topology. We have also examined reaction dynamics on potential energy surfaces with two minima, where the height of the intermediate isomerization barrier controls the reaction rate through an entropic bottleneck. We have focused on the exchange and abstraction reactions of vibrationally excited NH_3^+ ions with D_2, producing NH_2D^+ and NH_3D^+, respectively. Studies at a collision energy of 0.5 eV, with vibrational excitation ranging between 3.3 and 4.9 eV, have shown that the abstraction reaction is a direct process, while the exchange reaction proceeds through a collision complex. Proton transfer reactions are examples of reactions occurring on double minimum surfaces and are of general importance in combustion. We have recently tested the validity of the statistical hypothesis by observing flux distribution for decaying complexes. We are studying the reactions of O^- and OH^- with D_2, NH_3, and substituted allenes. We have studied metal cation-catalyzed elimination reactions of alkyl halides and aliphatic alcohols, demonstrating that the translational energy distributions are consistent with statistical dynamics, and that the lifetimes of the intermediate collision complexes are on the order of 100 femtoseconds. We are currently working on proton transfer reactions of O^- and OH^-, as well as a multiphoton ionization study of the neutral products of the electron detachment reaction between O^- and C_2H_4.

University of Southern California
Los Angeles, California 90089-0484

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

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

SRI International
Menlo Park, California 94025

238. Combustion Research Program: Flame Studies, Laser Diagnostics, and Chemical Kinetics
D.R. Crosley **$125,000**
Molecular Physics Laboratory

This research project involves a combination of laser-induced fluorescence (LIF) and chemical kinetics measurements to investigate the chemistry of hydrocarbon and ammonia combustion processes. The research comprises several related parts: (1) LIF probing of flat flames; (2) the development of an LIF spectroscopic and collisional data base; (3) computer modeling of combustion chemical networks; (4) development and application of rate constant estimation methods; and (5) a laser pyrolysis (LP)/LIF experiment. In LP/LIF, a mixture containing SF_6 is rapidly heated by a pulsed CO_2 laser, with time-resolved LIF measurements of radical concentrations, temperature, and excited level decay times. LP/LIF reaction rate measurements on $OH + CH_4$, C_3H_8, C_3H_6, and NH_3 have been made. Calculations on the $H + N_2O$ reaction and $CH_3 + CH_3$ recombination show bound intermediates and very different rate constant expressions from those currently used. The LIF spectroscopy of the $A^3\Pi_i$–$X^3\Sigma^-$ system of NH in a flow system has yielded lifetimes and transition probabilities. Quenching of the excited state has been studied at elevated temperature in the LP/LIF system. A rotational level dependence of the NH quenching cross section has been found in discharge flow experiments at room temperature. Quenching of electronically excited OH by NH_3 has been studied at room temperature in the flow system and at high temperature in LP/LIF. The LIF flame spectra of NH_2 in NH_3–O_2–N_2O flames are being cataloged. Quenching and energy transfer in the NS radical have also been studied.

Stanford University
Stanford, California 94305

239. Combustion Gas Spectroscopy Using Tunable Lasers
R.K. Hanson **$76,000**
Department of Mechanical Engineering

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

240. The Kinetics of Cyano Compounds at High Temperature
R.K. Hanson, C.T. Bowman **$78,000**
Department of Mechanical Engineering

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

University of Wisconsin
Madison, Wisconsin 53706

241. Unimolecular Reaction Dynamics
F.F. Crim **$79,110**
Department of Chemistry

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

Atomic Physics

Atlanta University
Atlanta, Georgia 30314

242. Theoretical Investigation of Electron–Ion Interaction
A.Z. Msezane **$57,000**
Department of Physics

The purpose of this project is to identify and calculate dominant physical mechanisms underlying the processes of electron impact excitation and ionization of ions, using the close-coupling approximation. Both total and differential cross sections are calculated and compared with measurements. In particular, detailed numerical studies are carried out to investigate the extent of contribution of the physical processes of inner-shell excitation-autoionization and inner-shell resonant excitation-double autoionization to the total ionization cross section of Ti^{+3}, important in CTR plasmas. Total and differential cross sections for electron impact excitation of magnesium(II) and cadmium(II), important in the He–Cd(II) hollow-cathode laser, are compared with measurements from energy loss spectrum and line emission data. An accurate configuration interaction wave function of the target is used to give the energy splittings between the ground state and the various excited states of interest very close to the observed values and the same values for the oscillator strengths in the length and velocity formulations.

California State University-Fullerton
Fullerton, California 92634

243. Correlated Processes in Atomic Collisions
J.M. Feagin **$37,900**
Department of Physics

A series of investigations is under way to better understand Coulomb correlations in atomic collisions. The goal is to engage in calculations that closely confront theory with experiment in a simple direct way. Much of the effort involves extensions of work on bound two-electron Wannier states, including a molecular orbital description of two-electron atoms and an application of quantum diffusion to Coulomb three-particle systems. At higher energies, ion–atom collision cross sections are being calculated for processes involving two or more electrons, especially for transfer and excitation.

College of William and Mary
Williamsburg, Virginia 23185

244. *Collisional Detachment of Negative Ions*

R.L. Champion, **$88,000**
L.D. Doverspike
Department of Physics

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

University of Colorado
Boulder, Colorado 80309-0440

245. *Spectroscopic Diagnostics of Electron–Atom Collisions*

A.C. Gallagher **$90,320**
Joint Institute for Laboratory Astrophysics

An experiment that measures cross sections for electron excitation of metal atoms is under way. The experiment yields differential cross sections for spin and angular momentum changes as a function of electron-scattering angle. The experiment uses lasers to excite atoms, first excited by electron collision, to high values of n. Fluorescence from a beam of these atoms in a magnetic field is detected. Each sublevel excited by the electrons is spectrally resolved, so that 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. Measurements of Na $3S(M'_s) \rightarrow 3P(M_s,M_L)$ excitation are under way, utilizing $3P \rightarrow 5S$ excitation by a tunable laser. Excellent signal-to-noise ratios have been obtained, and final apparatus improvements are under way to allow accurate measurement of this and other electron–sodium cross sections.

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

S.J. Smith **$96,600**
Joint Institute for Laboratory Astrophysics

This research is directed to the measurement of photon absorption by atoms immersed in very intense laser radiation fields of wavelengths near an atomic resonance. A primary objective is the accurate comparison of atomic absorption in a strong monochromatic field with the absorption in a strong field on which statistically well-characterized fluctuations are superimposed. A hybrid system of electro-optic and acousto-optic modulators is used to impose laser bandwidths up to 30 MHz and bandshapes out to 1 GHz from line center on a single-mode laser beam. Lineshapes ranging from Gaussian to Lorentzian are synthesized by controlling the time scale of the fluctuations. Measurements are in progress on the influence of such phase/frequency fluctuations on the zero-field Hanle effect in Yb^{174}. Measurements of the dependence of the resonance fluorescence power spectrum in atomic sodium on these fluctuations will be attempted. A study of the effects of amplitude fluctuations in two-photon absorption has been initiated.

Cornell University
Ithaca, New York 14853

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

V.O. Kostroun **$259,900**
Nuclear Science and Engineering Program

The project objectives are (1) to characterize experimentally the fundamental processes that take place in low-energy, very highly charged ion–atom collisions; (2) to obtain accurate total and differential cross-section data for these processes; (3) to investigate one- to four-electron, two-center collision systems in a systematic manner; and (4) to extend such studies to many-electron systems. Bare nuclei and hydrogen- and helium-like projectiles are furnished by the Cornell Electron Beam Ion Source, CEBIS, which produces such species by sequential electron impact ionization of ions trapped in an energetic, high-current-density electron beam. CEBIS is a superconducting solenoid cryogenic electron beam ion source, the first of its kind to be constructed in the U.S. At present the source produces bare nuclei of carbon, nitrogen, oxygen, and neon; and argon ions up to Ar^{11+} in a 6.5 keV, 0.5 A, and 1000 A/cm^2 electron beam in one millisecond. During the past year, an experimental apparatus was constructed to use the low-emittance, low-energy spread ion beams extracted from CEBIS in high-resolution collision spectroscopy of electron capture processes by highly charged ions colliding with hydrogen, helium, and heavier atoms at kinetic energies less than 2.5 keV/nucleon. The apparatus is capable of measuring inelastic energy losses, the energy and/or angular distributions of scattered and recoil particles, and the energy distribution of electrons emitted in ion–atom collisions.

University of Georgia
Athens, Georgia 30605

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

T.G. Heil **$53,800**
Department of Physics and Astronomy

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

Georgia Institute of Technology
Atlanta, Georgia 30332

249. *Statistical Fluctuations in Lasers*
R. Roy **$59,830**
School of Physics

Through experiment and theory the statistical properties of single mode and multimode dye laser radiation are investigated. The first passage time (FPT) technique is used to measure the contributions of pump and quantum noise to the intensity fluctuations. A numerical model will be developed to assess the dependence of the laser linewidth on these noise sources. Time scales of noise sources are quantitatively determined by studies of the noise power spectra of both the pump argon laser and the dye laser. The number of modes in the laser radiation are carefully controlled by Fabry-Perot etalons; and the effect of mode interactions on steady-state and transient fluctuations is studied. Our FPT technique is expected to quantitatively detect quantum noise in the presence of external noise that is six orders of magnitude larger. External noise is measured over time scales from a tenth of a microsecond to seconds. Information obtained from these studies will be relevant to the use of lasers in spectroscopy, nonlinear optics, and optical communication and computation. The fluctuations of a laser from the steady state and in transient growth determine the range of laser applications. Our studies will also be relevant to precision interferometric measurements and will help delineate the limits of accuracy and speed of these methods.

250. *Metastable Enhancement of C^+ and O^+ Capture Reactions*
E.W. Thomas **$76,920**
School of Physics

Beams of known metastable and ground-state C^+ and O^+ ions will be used to measure electron capture reactions in H_2, He, and H at energies from 20 to 1,000 eV. Focus is on $O^+ + H \rightarrow O + H^+$, where the reaction is accidentally resonant when the O^+ is in the metastable state. The reaction should have a very large cross section at low energies, and is a challenging problem for theoretical treatment. The general technique for preparing the ion beam involves controlled electron impact ionization. Below a known energy only ground-state species are possible; above that energy a mixed metastable-to-ground-state species is created. The ratio of metastable to ground-state species will be determined by a well-established technique involving the differing attenuation of the two species in a gas cell. We will also study how the metastable species of C^+ and O^+ interact with surfaces. Secondary electron ejection by potential processes is governed in part by exchange processes and should differ greatly between metastable and ground states. Chemical erosion of carbon by O^+ will also be studied to determine whether the initial excited state of the O^+ influences the erosion rate. This may determine whether chemical erosion processing of surfaces used by the microelectronics industry can be enhanced by preliminary excitation of the projectile species.

Harvard University
Cambridge, Massachusetts 02138

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

Cross sections have been calculated for transitions between the fine-structure levels of the n = 2 excited states of hydrogen-like ions induced by proton and electron impacts. The intensity ratio determined for the Lyman alpha doublet lines may be used as a diagnostic probe of the proton density and temperature in plasmas. Similar calculations for helium-like ions are in progress. Charge transfer cross sections for Fe^{2+} and Ni^{2+} in hydrogen have been obtained. Charge transfer ionization was found to be rapid for Fe^+ but not for Ni^+. Thus, their relative abundance in plasmas may provide a measure of the hydrogen content. Mutual neutralization of positive alkali metal ions and negative halogen ions was investigated. A wide range of efficiencies was found to be possible depending upon the specific participating species. The stability of multiply charged molecular ions has been examined using a formulation that goes beyond conventional theories.

Jackson State University
Jackson, Mississippi 39217

252. *Velocity Modulation Electronic Absorption Spectroscopy*
B.C. Hale **$47,650**
Department of Chemistry

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

University of Kansas
Lawrence, Kansas 66045

253. *Theoretical Studies of Many-Body Processes in Atomic and Molecular Physics*
S.-I. Chu **$71,400**
Department of Chemistry

The fundamental goal of this project is 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-Hermitian Floquet method for intensity-dependent continuum threshold shift and above-threshold multiphoton ionization; (3) most probable path approach for selecting the most important multiphoton excitation path, using artificial intelligence algorithms, allowing the study of multiphoton dynamics to very high order; (4) coupled dressed-quasi-molecular-states approach for the study of laser-assisted charge transfer reactions in slow ion–atom collisions; (5) SU(N) dynamical symmetries and symmetry breakings in multiphoton processes; (6) Floquet-Liouville super-matrix approach to multiphoton resonance fluorescence and multiple-wave mixings; and (7) multiphoton dynamics in Rydberg atoms.

Kansas State University
Manhattan, Kansas 66506

254. Atomic Physics of Strongly Correlated Systems

C.-D. Lin **$104,000**
Department of Physics

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

255. Atomic Physics with Highly Charged Ions

P. Richard **$1,000,000**
Department of Physics

High-velocity, highly charged ions produced by the 6 MV KSU tandem Van de Graaff accelerator are used to study single- and multielectron processes involving charge transfer, ionization, and excitation in ion–atom collisions. Direct electron capture (DC) and transfer ionization (TI), by highly charged ions, are studied at very low projectile velocities using recoil ion sources. Work continues on the study of the angular distributions of DC and TI for many systems including O^{+2} + He, Ar^{+q} on Ar, D_2 and H_2, and C, N, O, F, and Ne ($q \leq 8$) on He. The data are replete with oscillatory structures. The distributions provide much information on the character of the potential curves and are an excellent test of theoretical calculations for collisions at these energies. Single-electron capture by few-electron projectiles in He, H_2, and atomic hydrogen targets is being measured. Quasi-resonant multiple-electron transfer in near-symmetric F^{+q} + Ne systems is also being measured. Measurements of total cross sections for multiple ionization by relativistic uranium ions were performed at the Berkeley BEVALAC. The recoil ion source technology is being applied to the study of molecular ion chemistry. The fragmentation of CH_4 in collisions with fast highly charged ions is being studied. The cross sections for the production of CH_4^+, CH_3^+, CH_2^+, CH^+, and C^+ are measured and compared to a calculation including the two mechanisms of postcollision rearrangement and direct production. Theoretical calculations of the total cross section, n,ℓ distributions, and polarization from electron capture at high velocity are in progress. Calculations of theoretical lifetimes, transition energies, and branching ratios have been carried out for two-electron ions for configurations involving both electrons above the K shell.

Louisiana State University
Baton Rouge, Louisiana 70803-4001

256. Electron Collisions with Positive Ions

R.J.W. Henry **$62,980**
Department of Physics and Astronomy

The fundamental goal of this project is to delineate the important physical processes governing electron impact excitation processes for impurity ions in high-temperature plasmas of interest in thermonuclear reactors. The energy range considered is from the threshold to approximately four times the ionization energy. Calculations are based on a close-coupling expansion, which includes the important physical effects of electron exchange and resonances. Accurate target functions for the lowest three configurations of Fe^{+11} have been developed. Comparison of oscillator strengths and energy levels with other available calculations showed good agreement. For oxygen-like krypton, accurate target functions for the lowest configurations involving the $n = 2$ and $n = 3$ excited states were used in a close-coupling expansion. In general, coupling between different n levels was found to be weak. However, coupling effects among the $n = 2$ channels was found to be strong. Calculated cross sections for the low-lying $^2P^0$ and ^2D excited states of copper exhibit a rich resonance structure.

University of Louisville
Louisville, Kentucky 40292

257. Spectroscopic Studies of Hydrogen Atom and Molecule Collisions

J. Kielkopf **$68,500**
Department of Physics

This is an experimental study of the processes that occur during binary collisions in which one partner is an excited hydrogen atom or hydrogen molecule. For the molecule, selective excitation with a laser or by electron impact is followed by spectroscopic measurements that track the redistribution to other excited states. For the atom, observations of radiative collisions with both laser and dispersive methods probe the spectral line profile. The wings of the atomic spectral lines, formed by emission or absorption during the collision, are sensitive to the kinetic energy of the initial states, nonadiabatic state changes, and interference phenomena. The line cores are subject to collisional narrowing, nonadiabatic processes, asymmetries, and the effects of deviation from classical trajectories. Some of these effects are more significant with hydrogen than with other atoms because of its low mass and the degeneracy of its energy level structure. It is also possible to determine the interactions from spectral line wings directly, including the effects of many-body interactions in which the radiator collides simultaneously with two or more perturbers. The goal of this project is to use these data to elucidate the basic processes that affect the formation of spectral lines.

National Bureau of Standards
Boulder, Colorado 80303

258. *Atomic and Molecular Collision Processes*
D.W. Norcross **$92,000**
Quantum Physics Division

This project studies the physics of low-energy collisions of electrons with atoms, ions, and molecules, with an emphasis on detailed computational studies of fundamental processes involved in laser and fusion plasmas. Recent progress includes: (1) general code development to include nuclear dynamics and exchange effects more rigorously and to obtain bound states of molecular negative ions; (2) preliminary calculations for vibrational excitation of H_2 and HF; and (3) new calculations of inelastic scattering of electrons by Be^+. Our latest results for vibrational excitation of HF are in good agreement with $v = 0$ to 1 measurements even very near threshold, where complete treatment of nuclear dynamics removes remaining discrepancies. The facility to obtain energies of molecular negative ions will complement our results for resonance energies in HF and HCl, and in the isoelectronic molecules N_2, HCN, and CO. In the area of electron collisions with atomic ions, we have added strength to our earlier contention that a serious discrepancy between theory and measurements for excitation of Be^+ must be decided in favor of theory.

National Bureau of Standards
Gaithersburg, Maryland 20899

259. *Electron–Atom Collision Studies Using Optically State-Selected Beams*
R.J. Celotta, M.H. Kelley **$73,500**
Radiation Physics Division

The study of electron–atom collisions is greatly enhanced by the introduction of state selection in experimental investigations. The detailed information obtainable when all quantum mechanical variables are resolved makes possible a critical evaluation of theoretical methods at the most demanding level. By making use of new technologies for production of spin-polarized electrons (GaAs source) and state-selected sodium atoms (laser optical pumping), this project effectively achieves completely state-selected initial conditions for the combined incident electron-atomic target system. Initial studies have been completed of superelastic scattering, in which the electron-impact excitation of pure angular momentum states of Na(3P) by polarized electrons was investigated. Some elastic scattering results have also been obtained, in which spin-polarized electrons were scattered from spin-polarized sodium atoms in the ground state. The first direct observation of simultaneous spin-orbit and exchange effects in electron–atom scattering resulted from this work. Future research may include in-depth investigations of superelastic scattering over a large range of scattering angles and incident energies, a comprehensive study of the relative roles played by spin-orbit and exchange effects in elastic scattering, work toward including state-selected detection, and preparation to achieve the so-called perfect scattering experiment.

University of Nebraska
Lincoln, Nebraska 68588-0111

260. *Hyperspherical Coordinate Theory of Two-Electron Atomic Processes*
J.H. Macek, A.F. Starace **$69,000**
Department of Physics and Astronomy

The main focus of this project is the theoretical study of the effect of electron correlations on atomic collision processes. The theoretical approaches taken are primarily those based on the hyperspherical coordinate description of many-body systems. A major aim of the project is to lay the ground work for state-of-the-art calculations of collision cross sections using hyperspherical coordinate methods. Applications are made to specific atomic collision processes relevant to energy-related research in cases where a hyperspherical coordinate point of view can significantly contribute to understanding the underlying physical mechanisms. Recent progress involves the following topics: (1) bypassing translation factors in molecular dissociation and reactions; (2) three-body loosely bound states; (3) propagation of adiabatic channel functions; (4) comparison of hyperspherical and molecular descriptions of two-electron atoms; (5) contribution of $H^*(n = 2)$ states to H^-–He detachment collision cross sections; and (6) theory of anisotropy transfer and calculations of alignment of np states populated in electron capture by highly charged ions.

University of New Mexico
Albuquerque, New Mexico 87131

261. *Relativistic Atomic Beam Spectroscopy*
H.C. Bryant **$50,000**
Department of Physics and Astronomy **(7 mo.)**

A very high quality beam of relativistic H^- ions and laser fluxes and fields, impossible to produce under the usual laboratory conditions, are used to study the atomic physics of H^O and H^-. Strongly Doppler-shifted laser beams excite and probe states in H^O and in the doubly excited resonance structure of H^-, allowing observation of the effects of very large fields in the moving frame produced by the relativistic transformation of modest magnetic fields. Time dilation and the near-luminal velocities of excited atoms permit the measurement of lifetimes and nonexponential decay normally not accessible by spectroscopic methods. The search for the mechanism where two electrons are ejected from the H^- system by a single photon will be continued, using a technique that detects highly excited double resonances in H^-. Further study is planned for the recently discovered "atomic double beam interferometer" mechanism in the photodetachment cross section of H^- in an electric field. Techniques advanced by this project will be applied to check the validity of the special theory of relativity, using precisely known energy levels in atomic hydrogen.

Pennsylvania State University
Lehman, Pennsylvania 18627

262. *Electron Transfer, Ionization, and Excitation in Atomic Collisions*

T.G. Winter **$30,900**
Department of Physics

Electron transfer, ionization, and excitation in collisions of one atom (or ion) with another are studied theoretically. Emphasis is on accurate descriptions of collisional mechanisms for systems with few electrons; a middle range of energies (keV) is considered. The projectile's speed is then not very different from the average orbital speed of the active electron in the target atom (or ion). Therefore coupled-state methods are the most fruitful. The first calculation, recently completed, deals with collisions between protons and the hydrogenic ions He^+, Li^{2+}, Be^{3+}, B^{4+}, and C^{5+}. A coupled-Sturmian-pseudostate approach has been taken, which allows for continuum intermediate states that must be accounted for. The Sturmian approach has been shown to yield a very accurate description of the collisions. The calculation provides an understanding of an entire set of fundamental collision processes not previously studied systematically, either theoretically or experimentally, at keV energies. Results for another basic ion–atom collision have also recently been reported: differential cross sections for electron transfer and elastic scattering in the collision between an alpha particle and a hydrogen atom at keV energies.

Purdue University
West Lafayette, Indiana 47907

263. *Nonlinear Optical Interactions Involving the Real Gaussian Field*

D.S. Elliott **$54,890**
School of Electrical Engineering

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

Rice University
Houston, Texas 77005

264. *Theoretical Atomic and Molecular Sciences*

N.F. Lane **$106,000**
Department of Physics

Theoretical methods are applied to a broad range of collision processes involving electrons, atoms, molecules, and ions, in order to predict important new basic phenomena, to assist in the interpretation of experimental results, and to provide data where direct measurement is not possible. Current activities emphasize: (1) state changing in collisions of Rydberg atoms (intermediate n and ℓ) with atoms and molecules; (2) cross sections and coherence parameters for charge-transfer collisions of ions with atoms and molecules, including clusters; (3) role of core-excited autoionization states in Penning ionization of potassium and rubidium by metastable helium atoms; and (4) collision ionization of stripped ions in high-density, high-temperature plasmas.

University of Rochester
Rochester, New York 14627

265. *Nonlinear Optics with Broad-Band Lasers*

M.G. Raymer **$66,000**
Institute of Optics **(9 mo.)**

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

Smithsonian Astrophysical Observatory
Cambridge, Massachusetts 02138

266. *Measurements of Ionization Balance Parameters in Atomic Ions*

J.L. Kohl **$91,000**
Division of Atomic and Molecular Physics

An inclined electron/ion beams experiment has been developed to measure absolute dielectronic recombination (DR) cross sections as a function of the extrinsic electric field. The DR event rate is measured by detecting two products of DR in delayed coincidence: (1) the stabilizing photon and (2) the recombined ion. This technique discards events from charge transfer, which occur 10^7 times more frequently than DR. Recent results for the energy-averaged DR cross section in C^{3+} for a 10 V/cm extrinsic field indicate agreement with theoretical predictions to within a factor of two. This work provides the first opportunity to compare DR measurements for the same species by two groups that use different experimental techniques. To establish the reliability of the apparatus for the DR experiments, the absolute detection efficiencies and the overlaps of the beams were verified with measurements of charge transfer and electron impact excitation. The results of those measurements agree with well-established experiment and theory. Following the initial measurements, several major improvements were made that will increase signal levels by a factor of 18 and will significantly increase the stability of the ion beam.

St. John Fisher College
Rochester, New York 14618

267. Multilevel Relaxation Phenomena and Population Trappings
F.T. Hioe **$70,000**
Department of Physics

This project is directed toward the studies of multiphoton and multilevel coherent effects in laser-induced excitation of atomic and molecular systems. The newly discovered dynamic symmetries will be extended to a systematic classification of all possible SU(N) dynamic symmetries, and will be used to study systems involving continual as well as discrete energy levels, particularly multiphoton absorption above ionization threshold. Analytic solutions for four-state systems will be derived in relation to the study of quantum interference effect. The presence or absence of chaos and phase transitions in multimode lasers will also be explored.

University of Tennessee
Knoxville, Tennessee 37996-1200

268. Production and Destruction of Metastable Negative Ions
D.J. Pegg **$48,000**
Department of Physics and Astronomy

The project objective is to investigate the production and destruction of metastable negative ions. A fast-moving beam of negative ions is produced from a beam of incident positive ions by double-electron capture collisions in an alkali vapor cell. We have investigated the production of Ca^- ions following $Ca^+ +$ Li collisions over a particle energy range from 20 to 100 keV. We have also used autodetachment spectroscopy to study the structure of metastable Be^- and He_2^- ions. In this work discrete energy electrons that spontaneously detach themselves in flight from fast-moving negative ions are collected in the forward direction and energy-analyzed in an electron spectrometer. Our measurements on the negative ion dimer, He_2^-, indicate that we are observing the breakup of this ion by two distinct mechanisms. Our future plans include (1) studying the structure of alkaline-earth metastable negative ions (such as Ca^-) by photodetachment spectroscopy, and (2) using autodetachment spectroscopy to look for Ar^- metastable ions.

University of Texas
Austin, Texas 78712

269. Kinetic Studies Following State-Selective Laser Excitation
J.W. Keto **$86,000**
Department of Physics

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

Texas A and M University
College Station, Texas 77843

270. X-Ray Emission in Heavy-Ion Collisions
R.L. Watson **$76,000**
Cyclotron Institute

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

University of Toledo
Toledo, Ohio 43606

271. Semiempirical Studies of Atomic Structure
L.J. Curtis **$40,000**
Department of Physics and Astronomy

Studies of the structure and properties of very heavy and very highly ionized atoms that often occur as contaminants in high-temperature plasmas are carried out, using a combined program of experimental measurements, semiempirical data parameterizations, and *ab initio* computations. Spectroscopic classifications often require accuracies exceeding parts per million, which are not achieved by standard *ab initio* methods. Semiempirical systematizations can provide these accuracies, and a large and precise data base is available through recent studies using fast ion beam excitation, laser- and tokamak-produced plasmas, astrophysical sources, and conventional spectroscopic sources. These large blocks of data are being systematized and parameterized along isoelectronic, homologous, isoionic, Rydberg, and yrast series for the exposition of predictive empirical regularities. Trends revealed are then tested through well-chosen experimental measurements, and *ab initio* methods used to seek quantitative understanding of the empirical regularities. Recent work has included predictive studies of the copper, zinc, gallium, bromine, cadmium, and samarium isoelectronic sequences, and time-resolved fast ion beam measurements of spectra of highly ionized members of the neon sequence. The systematics of the sequences studied has been further investigated through large-scale calculations using the MFE CRAY X-MP computer.

Vanderbilt University
Nashville, Tennessee 37235

272. Theoretical Studies of Atomic Transitions
C. Froese Fischer **$94,000**
Department of Computer Science

The present research is part of an ongoing project in atomic structure calculation, with special emphasis on the prediction of energy levels and transition probabilities as well as lifetimes. The method used is the MCHF method for including correlation effects in the wave function, optionally corrected for relativistic effects in the Breit-Pauli approximation. Transitions of current interest are the forbidden transitions that may be important in astrophysics for the electron density, or that have been observed in tokamak plasmas and in transitions from Rydberg series. The present general purpose programs for the study of bound–bound transitions are being extended to include photoionization studies that may be characterized as bound–continuum transitions. Numerical procedures appropriate for supercomputers are being investigated to improve the accuracy of theoretical predictions.

University of Virginia
Charlottesville, Virginia 22901

273. Studies of Autoionizing States Relevant to Dielectronic Recombination
T.F. Gallagher **$94,000**
Department of Physics

We are investigating the relevant properties of autoionizing states, using a novel laser excitation scheme that is precisely the inverse of dielectronic recombination, which plays an important role in radiative power losses in tokamaks. We have recently concentrated on measuring the total autoionization rates of Sr 5pnℓ states as a function of n and ℓ, and have measured the angular and energy distributions of the ejected electrons. The latter measurements (1) provide more insight into the dynamics of autoionization and (2) determine the fraction of the autoionization that occurs in excited states of the ions, which is important in dielectronic recombination. To represent these data in a coherent fashion, we have extended multichannel quantum defect theory to incorporate our total autoionization rate measurements and the electron spectroscopy results. Current focus is on experiments in which microwave fields will be introduced to mimic the time varying plasma microfields. These investigations allow us to explore in detail the physics of dielectronic recombination in plasmas.

Western Michigan University
Kalamazoo, Michigan 49008-5151

274. Correlated Charge-Changing Ion–Atom Collisions
E.M. Bernstein, J.A. Tanis **$70,000**
Department of Physics

The project objective is to probe fundamental atomic interactions in collisions between ions and atoms. Individual processes of excitation, ionization, and charge transfer, and certain combinations of these processes, are investigated for highly charged ions incident on neutral gas targets by correlating outgoing projectile charge states with x-ray emission or with charge states of recoil target ions. This work uses accelerators at Lawrence Berkeley Laboratory, Brookhaven National Laboratory, Argonne National Laboratory, and Western Michigan University. A major effort to date has been the study of excitation and charge transfer occurring together in a single encounter with a target atom. This capture and excitation can be a correlated process, called resonant transfer and excitation (RTE), or an uncorrelated process, referred to as nonresonant transfer and excitation (NTE). In addition to RTE and NTE, other single-collision interactions involving two-electrons are being investigated: (1) two-electron capture, (2) two-electron loss, and (3) simultaneous excitation and loss. Total cross sections for capture and loss of a single electron are obtained along with the two-electron data, and considerable new data have been accumulated for these single-electron processes for a wide range of projectile energies and charge states.

Chemical Energy

Brigham Young University
Provo, Utah 84602

275. Metal–Support Interactions: Their Effects on Catalytic Properties of Cobalt
C.H. Bartholomew **$109,000**
Department of Chemical Engineering **(16 mo.)**

Metal–support interactions and their effects on adsorption, activity-selectivity, and electronic 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_2 adsorption properties; and (3) to measure directly the extent of interaction of various supports with iron and cobalt using Mossbauer spectroscopy. The work features a comprehensive, quantitative experimental investigation of cobalt on Al_2O_3, SiO_2, TiO_2, MgO, and carbon supports including careful characterization of the physical and chemical, bulk and surface properties of each catalyst with BET, H_2 and CO chemisorptions, XRD, TEM, TPD, and TPR measurements. Recent results provide evidence that dispersion and support significantly influence electronic, adsorption, and CO hydrogenation activity-selectivity properties of cobalt. For example, CO TPD experiments indicate that the binding energy of CO with cobalt varies with support, reduction temperature, and metal loading. The rate of CO dissociation and CO hydrogenation are also functions of support, metal loading, and pretreatment.

University of California
Irvine, California 92717

276. *Synthesis and Chemistry of Yttrium and Lanthanide Metal Complexes*

W.J. Evans **\$85,000**
Department of Chemistry

The goal of this research is to develop the special properties of complexes of yttrium and the lanthanide metals (14 heavy metals mined in California), which will allow the design and synthesis of materials with unique chemical, physical, and catalytic properties. Our studies of lanthanide–carbon bond reactivity in cyclopentadienyl complexes have provided the first molecules containing lanthanide–hydrogen bonds, and have shown how lanthanide-based reactivity can be precisely controlled by changing steric saturation in these complexes. This provides a basis for highly selective reactivity since 14 metals are available that vary gradually in size. By use of alkoxide and oxide co-ligands with and in place of cyclopentadienyl co-ligands, we have obtained durable polymetallic complexes that should allow practical exploitation of lanthanide-based reactivity in molecular frameworks that may model metal oxide catalysts and catalyst supports. These polymetallic complexes remain intact during reactions and can be studied definitively to learn about metal oxide surfaces and to develop new types of selective catalytic activity.

University of California
Santa Barbara, California 93106

277. *Homogeneous Catalysis of the Water Gas Shift Reaction*

P.C. Ford **\$89,000**
Department of Chemistry

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 oxyanions HO^- and CH_3O^- ($M\text{-}CO + RO^- \rightarrow M\text{-}CO_2R^-$), the decarboxylation of hydroxycarbonyl adducts ($M\text{-}CO_2H^- \rightarrow M\text{-}H^- + CO_2$), the reductive elimination of H_2 from metal hydrides ($M\text{-}H^- + H_2O \rightarrow H_2 + M + OH^-$), 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.

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

R.G. Pearson, P.H. Barrett **\$79,500**
Department of Chemistry

The goal of this project is to study the reactivity of metal atoms and small clusters with molecules in low-temperature matrices. Mossbauer and infrared spectroscopies are used to identify the reaction products. Reactions between iron, Fe_2, and iron clusters, and low-temperature matrix-isolated molecules of N_2, NO, CO, C_2H_4, SO_2, CS_2, and C_6H_6 have been studied and the products identified. This investigation includes the search for bond-cleaving reactions of HX, some of which have been found. Reactions of CH_3X and O_2 are also under study. The new concepts of absolute electronegativity, $(I + A)/2$, and absolute hardness, $(I - A)/2$, are being studied to help predict the reactions of iron atoms with selected molecules.

California Institute of Technology
Pasadena, California 91125

279. *Fundamental Studies of Olefin and Acetylene Insertion Reactions*

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

This project involves fundamental studies of the mechanism and thermodynamics of olefin and alkyne insertion into metal–hydrogen and metal–carbon bonds. Reactions of olefins with hydride and alkyl derivatives of metallocenes of the general formula $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R$ and $(\eta^5\text{-}C_5R'_5)_2M(olefin)H$ (R = H, alkyl, alkenyl, alkynyl; R′ = H,Me; M = Nb,Ta) proved to be very clean and amenable to mechanistic studies. Relative ground state energies for $(\eta^5\text{-}C_5R'_5)_2M(olefin)H$ (M = Nb,Ta; R′ = H, CH_3) have been determined by competitive binding studies. The molecular structure of $(\eta^5\text{-}C_5Me_5)_2Nb(CH_2CHC_6H_5)H$ was determined by x-ray crystallography. Relative transition state energies were established by measuring the insertion rates as a function of the olefin and steric contributions from the metallocene (R′ = Me vs. H). The kinetics of stepwise insertion of ethylene into the scandium–carbon bond of $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R$ (R = alkyl) were examined by ^{13}C NMR spectroscopy. The reaction of $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R$ (R = Me) with alkynes, $RC{\equiv}CR'$ (R = Me; R′ = Me,Et,Ph,*i*Pr) and decomposition of $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R$ (R = Et,*n*Pr) via β-hydrogen elimination are being probed with ^1H NMR spectroscopy. These processes (olefin insertion into the metal–hydride bond, its inverse, β-hydride elimination, and the related process of insertion of olefins into the metal alkyl bond) are among the most important steps in homogeneously catalyzed reactions of olefins. The reaction of $(\eta^5\text{-}C_5Me_5)_2ScCH_3$ with alkynes $RC{\equiv}CR'$(R = CH_3;R′ = CH_3, CH_2CH_3, Ph, $CHMe_2$) was investigated using ^1H NMR spectroscopy.

280. *Catalytic Assembly of Hydrocarbons from Carbon Monoxide*

R.H. Grubbs **\$117,000**
Department of Chemistry

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

University of Chicago
Chicago, Illinois 60637

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

L.M. Stock **$191,000**
Department of Chemistry **(24 mo.)**

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

University of Colorado
Boulder, Colorado 80309

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

M.R. DuBois **$60,000**
Department of Chemistry and Biochemistry

The project objective is to study the hydrogenolysis of carbon–heteroatom bonds in cationic complexes of the general formula $[(C_5H_5Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]^+$. Complexes where R is a carbonyl-containing substituent have been prepared from bromoketones, bromoesters, and acyl halides. Hydrogen reacts with these complexes at room temperature to hydrogenolyze the carbon–sulfur bonds of the thiolate ligands. Final organic products are the corresponding ketones, esters, or aldehydes. The cations with acyl-thiolate ligands undergo a competing reaction with hydrogen, in which the carbonyl carbon–oxygen bond is hydrogenolyzed. The products have been identified as water and $[(CpMo)_2(S_2CH_2)(S_2CR)]^+$. An x-ray diffraction study of the latter complex has established that the cation is bridged by a planar dithioacetate ligand coordinated to one molybdenum ion through two sulfur donors, and to the second metal ion through both sulfurs and the adjacent carbon atom. Studies on this and related systems suggest that the hydrogen molecule is activated heterolytically to form a free proton and a complex with a hydrosulfido ligand. Both entities appear to be important in the subsequent cleavage of the carbon–heteroatom bonds. Further studies are in progress to establish the relevance of these systems as models for heterogeneous hydrotreating catalysts.

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

B.E. Koel **$71,250**
CIRES

This project explores the chemisorption and reactions of hydrocarbons on well-characterized, single-crystal bimetallic surfaces in order to understand the role of electronic and geometric effects in modifying the chemistry of these surfaces. Recent work has included studies of three important systems: (1) C_2H_4–K–Pt(111), (2) C_2H_4–Bi–Pt(111), and (3) C_2H_4–Pd–Nb(110). Potassium coadsorption causes the formation of a new, weakly bound state of C_2H_4 in TPD, and we have identified the origin of the state as a pi-bonded species, using HREELS. At high potassium coverages, the mechanism for C_2H_4 decomposition no longer passes through a stable CCH_3 species, but now through a $CHCH_3$ species. Bismuth coadsorption acts to block platinum sites for C_2H_4 adsorption and decomposition, but does not affect the C_2H_4 binding energy. Work is in progress to model these results in order to determine surface ensemble requirements. The properties of palladium monolayers and thin films on early transition metal substrates are dramatically different from the surface properties of bulk palladium. The changes include a large rehybridization of the palladium atoms to a noble metal electronic configuration. We have recently performed TPD studies of C_2H_4 adsorption on Pd/Nb(110) surfaces, and found the chemisorption bond to be weakened substantially compared to that on bulk palladium surfaces.

Colorado State University
Fort Collins, Colorado 80523

284. *Chemically Modified Electrodes and Related Solution Chemistry*

C.M. Elliott **$81,000**
Department of Chemistry

The goal of this research is to develop chemistry that will allow us to alter the chemical and/or physical properties of the electrode–solution interface in useful ways. Our primary emphasis is the development of polymer-coated electrodes containing electroactive materials. We have developed several polymer systems of interest, and we are studying the fundamental processes of electron and ion transport in these materials. In the course of these studies, we have developed a new type of electronically conducting "organic" polymer, which is presently under study. This material is unique in many aspects when compared to other electronically conducting polymers. We have also prepared other polymer materials of potential catalytic interest that contain electroactive transition-metal complexes (e.g., metalloporphyrins). Aspects of our studies of chemically modified electrodes involve developing (1) methods for incorporating electroactive systems of interest into polymers and (2) molecules of potential interest (e.g., catalysts) for incorporation into polymer films. Different synthetic procedures appropriate for each material under study are investigated in order to chemically incorporate the molecules of interest into polymers. A number of novel metalloporphyrins have been prepared; their redox chemistry is investigated both in solution and polymer-bound. Other polymers under study have novel electrochromic and redox-adjustable ion-exchange properties. The primary methods of investigation are electrochemical, including such techniques as chronoamperometry, cyclic voltammetry, and rotated disk voltammetry.

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

J.R. Norton **$90,000**
Department of Chemistry

This project has developed several efficient general syntheses of diosmacycloalkanes. The project will next determine the extent to which these compounds can: (1) serve as models for methylene aggregation on the surface of Fischer-Tropsch catalysts; and (2) rearrange carbon skeletons. The properties of these compounds will be compared to those of their mononuclear analogs, in order to determine which (if any) steps in typical catalytic sequences require the presence of polynuclear systems. We have shown that, in contrast to the established chemistry of cyclobutane rings without metals, olefins exchange in and out of diosmacyclobutanes with retention of stereochemistry at carbon. This result helps to explain the lack of *cis–trans* isomerization frequently found when olefins are adsorbed on catalytic metal surfaces.

286. *Heterobimetallic Complexes for Carbon Monoxide Reduction*

J.K. Stille **$73,400**
Department of Chemistry

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

University of Connecticut
Storrs, Connecticut 06268

287. *Highly Dispersed Metal Atoms in Zeolites*

S.L. Suib **$73,000**
Department of Chemistry

Our research involves (1) the preparation and characterization of highly dispersed metal clusters in zeolites, (2) surface studies of zeolites, and (3) investigations of the poisoning of fluid-cracking zeolite catalysts by metals. All aspects of this research deal with the synthesis, characterization, and catalytic activity of zeolites. We have developed a synthetic method that uses a microwave plasma to decompose organometallic species in the pores of zeolites X and Y. Both iron and cobalt metal clusters have been produced as superparamagnetic particles of diameters less than 10 A. The samples have been characterized with Mossbauer, ferromagnetic resonance, electron paramagnetic resonance, microscopy, and chemisorption methods. These materials are selective Fischer-Tropsch catalysts for the production of light olefins. The second area studies surfaces of zeolites and phosphorus molecular sieves. Chemical state plots for aluminum, silicon, and phosphorus were assembled for a variety of zeolites with high and low Si/Al ratios. Oxygen ion polarizabilities were determined from x-ray-excited Auger transitions. Rutherford backscattering methods were also used to study surfaces of zeolites, to distinguish surface and bulk metal species. The final area involves the poisoning of fluid-cracking catalysts by metals. Vanadium poisons leach oxygen from the zeolite, destroying the lattice, while nickel aggregates overcrack the gasoline range hydrocarbons. Silica-rich fluid-cracking catalysts were also studied with surface science, luminescence, and microscopy methods. Other poisons like iron and copper are also studied.

University of Delaware
Newark, Delaware 19716

288. *A Surface Science Investigation of Potential Intermediates, Catalysts, and Promoters in the Synthesis of Higher Alcohols by Metals*

M.A. Barteau **$0**
Center for Catalytic Science and Technology **(15 mo.)**

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. We have demonstrated that, on the Pd(111) surface, alcohols decompose to $CO + H_2 +$ hydrocarbons one unit shorter than the parent alcohol. These reactions proceed via the sequence: alcohol to alkoxide to aldehyde to acyl to CO + hydrocarbon. This sequence is the reverse of that proposed for higher alcohol synthesis on the group VIII metals. Oxygen atoms on the surface play five different roles in alcohol conversion, including reducing the strength of aldehyde–surface bonds, permitting the intermediate aldehydes to desorb from the surface. Similar pathways are observed on Rh(111) although the relative rates of the various competing reactions differ, leading to changes in the product distribution. These results help to explain reaction mechanisms and promoter effects in both alcohol synthesis and selective oxidation.

289. *Characterization of Metal–Support Bonds in Supported Metal Catalysts*

B.C. Gates **$104,500**
Department of Chemical Engineering **(15 mo.)**

This research investigates the structure and bonding of "molecular" metal complexes of tungsten, rhenium, osmium, iridium, and platinum, bonded to the surfaces of metal oxides (MgO, γ-Al_2O_3, and SiO_2). These surface complexes will be synthesized from reactive organometallic precursors and characterized by EXAFS combined with temperature-programmed decomposition and reaction, FTIR, and ^{13}C and metal NMR spectroscopies. Results will lead to the elucidation of precise surface structures, including the nature and distance of the bonds between the metal and the oxygen ions of the support. The supported "molecular" complexes will be reduced gently in H_2, giving ultradispersed supported metals. EXAFS and the complementary techniques will be used to characterize the structures of these species, with focus on the metal–support interactions. The results are expected to provide (1) a foundation in molecular chemistry for understanding metal–support interactions and (2) some of the most nearly definitive structural data for ultradispersed metals.

Harvard University
Cambridge, Massachusetts 02138

290. *Model Studies of Hydrodesulfurization and Hydrodenitrogenation on Sulfided Molybdenum Surfaces*

C.M. Friend **$102,330**
Department of Chemistry

Model hydrodesulfurization reactions of four-, three-, and two-carbon cyclic and linear sulfur-containing molecules have been investigated on Mo(110) under ultrahigh vacuum conditions, using temperature-programmed reaction spectroscopy, isotopic exchange reactions, and Auger electron spectroscopy. The effects of the energetics of ring opening on the product distributions and energetics of desulfurization were investigated. Thiophene exclusively undergoes irreversible C–H bond activation on Mo(110). At low coverage, all thiophene decomposition occurs below 400 K. At high coverage, thiophene undergoes selective dehydrogenation at the α position with a hydrogen-bearing fragment stable on the surface up to 570 K. No volatile hydrocarbon products are observed in the thiophene reaction. In contrast, the fully saturated C_4S-ring, tetrahydrothiophene, yields butane and butene in the temperature range of 300 to 420 K, with the activation energy for butane formation $\sim$ 5 kcal/mole less than for butene formation. An analogous reaction with the same energetics is observed for 1-butanethiol on the Mo(110) surface with a product yield that is roughly five times greater than for tetrahydrothiophene. A general mechanism for the cyclic sulfides reaction on Mo(110) is proposed where one of the α-carbons is initially hydrogenated with accompanying C–S bond scission, producing a thiolate intermediate. Hydrogenation of the thiolate at the α-carbon yields butane while β-hydride elimination forms 1-butene. Deuterium coadsorption experiments and reactions of C_3-analogs substantiate this mechanism.

University of Illinois
Chicago, Illinois 60680

291. **In Situ** *Ultraviolet Diffuse Reflectance Studies of Heterogeneous Catalysis*

R.D. Gonzalez **$106,500**
Department of Chemical Engineering **(18 mo.)**

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

Indiana University
Bloomington, Indiana 47405

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

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

The catalytic conversion of synthesis gas to methanol promises to play a vital role in our nation's energy future. Preferred catalysts are now based on Cu–ZnO compositions, which are considerably more active than the separate components. The project objective is to develop a microscopic understanding of the role played by surface structure and composition in determining the activity and selectivity of Cu–ZnO catalysts for methanol synthesis ($CO + 2H_2 \rightarrow CH_3OH$). We believe such information will guide the design of improved catalysts for this important reaction. Our approach involves model catalysts prepared from single-crystal copper or by vapor-depositing copper onto low-index planes of a ZnO single crystal. In this way a range of well-defined surface electronic and geometric models of the Cu–ZnO catalysts can be prepared. These structures will be characterized in ultrahigh vacuum using a variety of surface analytical techniques immediately before and after high-pressure kinetic measurements, which are used to determine the activity of the model catalysts. The influence of surface modifiers and the kinetics of elementary reaction steps will also be studied. By correlating surface structure and composition with the observed rates, we should begin to develop a fundamental understanding of the surface chemical requirements for effective catalyst design.

293. *Metal Alkoxides: Models for Metal Oxides*

M.H. Chisholm **$95,000**
Department of Chemistry

Structural analogies between polynuclear metal alkoxides and metal oxides have been noted, with the former providing models for subunits within the extended networks of the latter. An extensive organometallic chemistry supported by alkoxy ligands is emerging. Their facile interconversion between terminal and bridging positions and between σ^2 and $(\sigma^2 + \pi^2)$ donors allows for easy uptake and release of substrate molecules. Key observations during the 1985 to 1987 period are: (1) the cleavage of $C{\equiv}O$ to carbido- and oxo-tungsten alkoxide clusters; (2) the coupling, co-coupling, and sometimes metathesis-like reactions ($M = W$) between $C{\equiv}C$, $C{\equiv}N$, and $M{\equiv}M$ bonds in $M_2(OR)_6$ compounds; (3) unusual α- and β-hydrogen effects in dinuclear alkyl-alkoxides of molybdenum tungsten; and (4) the isolation of Mo–Mo quadruply bonded compounds supported by alkoxide ligands. Recent developments have led to a general synthesis of hydridoditungsten alkoxide anions $W_2(\mu\text{-}H)(OR)_8^-$, which have been isolated as sodium salts. New nitrido and amido clusters have been discovered, $Mo_4(\mu_3\text{-}N)_2(OPr^i)_{12}$ and $W_3(\mu_3\text{-}NH)(OPr^i)_{10}$, which may provide models for the Haber synthesis of NH_3 from N_2 and H_2. Routes to alkyl/aryl-containing tri- and tetranuclear alkoxide clusters have been developed.

294. *A Model Approach to Vanadium in Crude Oils and Refining*

G. Christou **$171,700**
Department of Chemistry **(20 mo.)**

Crude oils contain several metal-containing impurities, particularly vanadium and nickel. The vanadium impurities may contain the metal bound to both porphyrin and non-porphyrin organic groups. During hydrodesulfurization (HDS) treatment, these vanadium compounds are converted to polymeric vanadium sulfide deposits that contribute to poisoning of the molybdenum HDS catalysts. A variety of small-molecular-weight vanadium–sulfide species may be formed on the catalyst surface as intermediates to the polymeric deposits. The project objectives are (1) to synthesize discrete vanadium sulfide species to model the materials forming under HDS conditions; and (2) to provide a mechanistic insight into the transformations described. Vanadium species with nuclearities up to four have been synthesized and structurally characterized. Reactivity properties are being explored, with particular emphasis on controlled conversion of small nuclearity materials into higher nuclearity materials. The preparation of mixed vanadium–molybdenum–sulfides is also being explored, to investigate whether such species are forming on the catalyst surface.

295. *Free-Radical and Concerted Reactions in Coal Liquefaction*

J.J. Gajewski, K.E. Gilbert **$78,000**
Department of Chemistry

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

Indiana University–Purdue University
Indianapolis, Indiana 46223

296. *Studies of Metal–Ammonia Interactions with Aromatic Substrates*

P.W. Rabideau **$69,000**
Department of Chemistry

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

University of Kentucky
Lexington, Kentucky 40506-0055

297. *Metallacumulenes and Carbide Complexes*

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

We are studying the synthesis, structure, and reactivity of metallacumulenes and carbide complexes containing cumulated chains of carbon–carbon double bonds terminating at transition metal atoms at one or both ends. Focus is on better understanding the behavior of surface carbides and derived fragments during carbon monoxide and acetylene conversion reactions on heterogeneous catalysts. We have achieved the synthesis of $[(Me_3CO)_3W{\equiv}C\text{-}Ru(C0)_2(Cp)]$, the first heterodinuclear μ_2-carbide complex, via the reaction of $[W({\equiv}CEt)(OCMe_3)_3]$ with $[Ru(C{\equiv}CMe)(CO)_2(Cp)]$, with concomitant elimination of 2-pentyne. The geometry of the bridging carbide ligand is linear (177°). We have observed the interconversion of alkyne and vinylidene ligands on molybdenum and tungsten centers. Electron-rich alkynyl complexes $[M(C{\equiv}CR')(L)(PR_3)_2(Cp)]$ are prepared by photolysis of $[W(C{\equiv}CR')(CO)_3(Cp)]$ with phosphines or phosphites, or by deprotonation of

$[Mo(HC{\equiv}CR')(PR_3)_2(Cp)]^+$ with strong bases in the presence of L (L = CO, phosphine, or phosphite). Electrophiles (EX = HPF_6, $MeOSO_2CF_3$, and so forth) add to these complexes to give vinylidene complexes $[M(C{=}CER')(L)(PR_3)_2(Cp)]X$. In certain cases, a second equivalent of HX adds to give alkylidynes $[M(C{=}CH_2R')X(PR_3)_2(Cp)]^+$. $[Mo(C{=}CHCMe_3)(CO)\{P(OMe)_3\}_2(Cp)]^+$ reverts to $[Mo(HC{\equiv}CCMe_3)\{P(OMe)_3\}_2(Cp)]^+$ above 0°C, whereas other vinylidenes are stable at room temperature. Reactivity, spectroscopic properties, crystal structures, and electrochemical properties of these and related iron and ruthenium complexes are under study.

Lehigh University
Bethlehem, Pennsylvania 18015

298. *Infrared Study of Carbon Deposits on Bimetallic Catalysts*

R.P. Eischens **$100,950**
Department of Chemistry

The project objectives are to determine the nature of carbon deposits on alumina-supported bimetallic catalysts and to determine whether the species that produce infrared bands at 1,585 and 1,460 cm^{-1} are related to the enhanced productivity of bimetallic catalysts. Preliminary results were interpreted on the basis that bands observed at 1,585 and 1,460 cm^{-1} were due to carbon–oxygen bonds even though the deposition of coke by exposure of the catalysts to hydrocarbons was conducted under reducing conditions. Later interpretations by other researchers assigned the 1,585 cm^{-1} band to the carbon–carbon stretching mode in aromatic rings and the 1,460 cm^{-1} band to a CH_2 deformation. The first phase involves isotopic substitution studies designed to definitively establish the nature of the species producing the 1,565 and 1,460 cm^{-1} bands. Results from deuterium substitution experiments are consistent with the carbon–oxygen bond concept. The second phase will involve studies of a number of bimetallic catalyst systems and the effect of sulfur, to determine whether the species producing the 1,585 and 1,460 cm^{-1} are especially detrimental to the performance of the kinds of catalysts used in petroleum-reforming processes.

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

K. Klier, G.W. Simmons, **$161,000**
R.G. Herman, J.E. Sturm
Department of Chemistry **(18 mo.)**

The object of this research is to lay scientific foundations for processes used for the selective oxidation of methane to useful energy chemicals and basic chemicals. Recent effort focused on a surface science study of the palladium(100)–oxygen–dichloromethane–methane system using LEED-Auger-mass spectrometry. Pd–O and P–CH_2Cl_2 reactions were characterized in detail, while the Pd–CH_4 reaction was not detected at pressures below 10^{-6} torr and temperatures below 1,000 K. Recent results of Auger lineshape analysis show that surface chlorine from dichloromethane adsorption is atomic in nature. Subsequent exposure of dissociatively adsorbed dichloromethane to oxygen with mild heating leads to the removal of all surface carbon in the form of CO and CO_2 (hydrogen apparently desorbs at room temperature) leaving the surface chlorine unchanged, unless heated above 1,000 K, whereupon chlorine desorbs. Importantly, the surface chlorine coverage shows a correlation with the CO, CO_2, and O_2 desorption temperatures and their relative amounts, suggesting that chlorine affects the oxidation of the carbon-containing fragments. Reacting methane with Pd–Cl, Pd–O, and Pd–CH_2Cl_2 surfaces is under study. A recently completed HREEL spectrometer is being used to identify surface species associated with the reaction of CH_2Cl_2 with palladium and subsequent reactions of this surface with oxygen and methane.

Louisiana State University
Baton Rouge, Louisiana 70803-7303

300. *Direct Alcohol Synthesis Using Modified Cobalt Catalysts*

G.L. Griffin **$48,000**
Department of Chemical Engineering

Fundamental studies involve preparation, characterization, and utilization of mixed Cu–Co–ZnO heterogeneous catalysts for the direct manufacture of methanol and higher molecular weight alcohols from synthesis gas mixtures (i.e., prepared by methane reforming or coal gasification). The goal is to understand and control the factors that determine the selectivity of the catalyst. We have prepared a series of binary and ternary compositions using both sequential and simultaneous coprecipitation sequences, both with and without alkali metal promoters. We use temperature-programmed desorption techniques to measure the concentration and adsorption energy of sites on the individual chemical components of these catalysts, with H_2, CO, and CH_3OH as adsorbates. Measured site concentrations are compared with values determined by conventional surface area determination techniques. We are measuring the catalyst activities for a series of reactions related to alcohol synthesis (e.g., CH_2O hydrogenation, CH_3OH and C_2H_5OH synthesis via CO hydrogenation, and C_2H_5OH synthesis via CH_3OH homologation). Results to date are consistent with a model in which higher alcohol synthesis occurs via a modified Fischer-Tropsch mechanism on chemically perturbed cobalt sites.

University of Louisville Research Foundation
Louisville, Kentucky 40292

301. *Synthesis and Properties of Metallocarboxylic Acids*

D.H. Gibson **$76,240**
Department of Chemistry

The goals of this project are (1) to develop general syntheses of metallocarboxylic acids (suspected intermediates in the water-gas shift reaction) and some of their derivatives; and (2) to establish the characteristic reactions of these compounds. An understanding of the chemistry of the metallocarboxylic acids also requires an understanding of the chemistry of their conjugate bases. We have devised a reliable synthesis of $CpFe(CO)(PPh_3)COOH$ and have prepared and isolated the corresponding lithium, potassium, and calcium salts of the acid. In studying the reactions of the salts, we have found that they are readily esterified by alcohols and easily alkylated to the corresponding methyl ester by methyl iodide or $CF_3SO_3CH_3$. They are oxide-transfer agents to trityl cation and to metal carbonyl cations, such as $CpFe(CO)_3^+$ and $Mn(CO)_5(PPh_3)^+$. Efforts are in progress to establish the crystallographic structures of some of the salts and to delineate their chemistry.

University of Massachusetts
Amherst, Massachusetts 01003

302. Surface Analyses and Modeling of Rate Multiplicity and Instabilities for NO Reduction on Platinum Foil

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

The project studies rate multiplicity, oscillations, and spatially nonuniform states. Our experimental goal is to develop a scanning Fourier transform infrared emission spectroscopic technique to measure *in situ* the spatial and time dependence of surface composition for test catalytic reaction systems (NO reduction by H_2 and CO on a platinum foil) with such kinetic instabilities. This technique will provide pertinent information about spatial communication and synchronization along the surface during an oscillatory state. Experiments will be conducted over a wide total pressure range in order to assess the influence of transport limitations and total pressure. An indirect catalyst-heating technique will be used to minimize surface-temperature nonuniformities. Gas composition will be monitored with a quadrupole mass spectrometer. An ESCA facility will be used to check the role of platinum surface impurities in causing irreproducibility and instabilities. Experiments will also include intermittent temperature-programmed NO and CO desorption and temperature-programmed NO reduction by H_2 and CO. Our modeling goal is to develop a new method of kinetic model discrimination for a reaction that exhibits a multiplicity of uniform states. Singularity theory techniques for analyzing reaction-transport multiplicity will be applied to intrinsic rate multiplicity, in order to determine the functional properties a model must have to qualitatively account for the multiplicity features. The method relies on construction of detailed rate multiplicity features, direct measurement of the surface composition for each of the multiple states, and transient studies of individual steps in the overall reaction sequence. We also plan to develop a method of fitting the models to the singular point data as a way of estimating kinetic parameters. *In situ* surface-state data is essential in this step.

Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

303. Chemistry of Bimetallic Cyclopentadienyl Complexes

R.R. Schrock **$167,540**
Department of Chemistry

We are exploring the chemistry of homo- and heterobimetallic complexes containing peralkylated cyclopentadienyl rings linked via a relatively flexible C_2H_4 bridge, to determine whether two linked metals can behave cooperatively in catalytic reactions in ways that cannot be duplicated in systems containing monometallic catalysts. We can prepare complexes containing tungsten linked to another tungsten, or to rhodium or cobalt. We have prepared and explored some chemistry of monomeric polyhydride complexes of tungsten, and discovered one reaction that occurs for dimeric hydride complexes that contain η^5-$C_5Me_5(Cp^*)$ ligands but not for an analogous polyhydride system containing a linked cyclopentadienyl system. The discovery of the first trimethyltungstacyclobutadiene complex by a reaction of 2-butyne with a $W{\equiv}W$ bond, may enable us to prepare simpler permethylated linked cyclopentadienyl systems. While exploring the possible reactions of Cp^* complexes that might lead to hydrides, we have extensively explored the chemistry of the WCp^* methyl system through the synthesis and characterization of complexes including WCp^*Me_4, $WCp^*Me_4^+$, WCp^*Me_5, and $WCp^*Me_3(CH_2)$. The end product of decomposition of many of the species in this general class is $[WCp^*Me]_2(\mu\text{-}CH)(\mu\text{-}CMe)$; an x-ray study showed it to contain a slightly bent W_2C_2 ring and cisoid Cp^* ligands. An x-ray study of $WCp^*Me_4^+$ showed it to be the only known $M(\eta^5\text{-}C_5R_5)L_4$ complex that is pseudotrigonal bipyramidal instead of tetragonal pyramidal. Focus is on (1) bimetallic complexes containing tungsten and iron, ruthenium, or rhenium; and (2) demonstrating that bimetallic complexes can undergo reactions with low probability in systems containing only monomeric species.

National Bureau of Standards
Gaithersburg, Maryland 20899

304. Structure and Reactivity of Chemisorbed Species and Reaction Intermediates

T.E. Madey **$280,250**
Surface Science Division **(10 mo.)**

This project involves the structure and reactivity of adsorbed molecules on single-crystal surfaces and on high area catalysts, using a variety of experimental methods. Recent research has involved the investigation of surface processes related to surface chemistry and catalysis. The role of surface additives (oxygen, bromine, alkali atoms) on the local structure and surface chemistry of small molecules (NH_3, H_2O, O_2, CO) adsorbed on single-crystal metal surfaces (ruthenium, iron, nickel, copper, silver) is studied using the electron stimulated desorption ion angular distribution (ESDIAD) method. The additives frequently are found to induce new structural forms of the adsorbed molecules and reaction products. A new digital-imaging ESDIAD system is being used to study the surface structure and chemistry of small molecules (H_2O, NH_3, HF) on planar and stepped silicon surfaces; unusual structures are identified for the dissociation products. Neutron inelastic scattering (NIS) is used to measure the vibrational spectra of adsorbed and subsurface hydrogen on high-area palladium black, and of NH_3 on zeolite catalysts. We also are studying chemisorption and catalytic activity on monolayer films of platinum on tungsten surfaces.

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

305. Mechanistic Examination of Organometallic Electron-Transfer Reactions

J.D. Atwood **$150,000**
Department of Chemistry **(16 mo.)**

This research involves determining the mechanisms of electron transfer between organometallic complexes. These processes are implicated in many synthetic and homogeneous catalytic reactions. A combination of kinetic studies of rapid reactions and electrochemical experiments (including stopped-flow infrared spectroscopy) is being used to unravel the organometallic reaction mechanisms of metal carbonyl complexes, to distinguish among inner sphere, outer sphere, and nucleophilic pathways for the electron transfer. The work will examine reactions between metal carbonyl cations and anions, between organometallic complexes and coordination complexes, and between metal–metal bonded complexes and metal carbonyl anions.

University of North Carolina
Chapel Hill, North Carolina 27514

306. *The Heats of Formation of Gas Phase Organosulfur Molecules and Applications of ^{17}O and ^{33}S NMR to Structure Determinations*

T. Baer, S.A. Evans, Jr. **$120,000**
Department of Chemistry **(18 mo.)**

This project emphasizes photoionization and heteronuclear nuclear magnetic resonance (NMR) techniques to determine structures and energetics of organosulfur molecules. The ΔH_f^o of the series: RS · [R = CH_3, CH_3CH_2, $(CH_3)_2CH$, and $(CH_3)_3C$] are measured. In addition, the ΔH_f^o of various sulfonyl compounds are determined by bomb calorimetry to make these substances amenable for photoionization studies. Chemical oxidation of sulfenyl sulfur (–S–) to sulfones ($-SO_2-$) and particularly, to sulfonic acids ($-SO_3H$) serves to quench the quadrupolar broadening effect. This allows for development of an analytical NMR technique for the rapid and accurate analysis of sulfur in organosulfur constituents in coal and petroleum extracts. Polar substituent effects on ^{33}S chemical shifts in aryl sulfones and sulfonic acids are evaluated, as well as the possible use of magic-angle spinning techniques for determination of ^{33}S shift parameters in the solid state.

307. *Reductive Coupling of Carbon Monoxide to C_2 Products*

J.L. Templeton **$40,000**
Department of Chemistry

Two approaches to reductive C–C bond formation between adjacent carbon monoxide ligands at a single metal center are being pursued. The first (recently validated by Lippard) employs external reductants in an effort to reductively couple *cis*-carbonyl ligands to form $[OC{\equiv}CO]^{-2}$. The acute OC–M–CO angles of seven-coordinate d^4 metal carbonyl derivatives and the six-coordinate d^4 alkyne-containing products are uniquely suited for this chemistry. The second approach focuses on the conversion of a terminal CO to a pseudocarbyne by protonation (or Lewis acid addition) at the oxygen to generate an effective hydroxycarbyne *cis* to a carbonyl. Examples of carbyne–carbonyl coupling have been reported, and we hope to promote a similar internal redox process by addition of acid and free ligand to convert d^6 $L_4M(CO)_2$ to $L_4L'M(HOC{\equiv}COH)$ or a Lewis acid analog.

Northwestern University
Evanston, Illinois 60201

308. *Solid-State, Surface, and Catalytic Studies of Oxides*

H.H. Kung **$100,000**
Department of Chemical Engineering

The emphasis of this project is on selective oxidation reactions of hydrocarbons catalyzed by oxidic materials, especially the selective oxidation of low-priced saturated hydrocarbon to unsaturated hydrocarbons, aromatics, alcohols, aldehydes, or acids that are of much higher value. Such reactions are especially demanding because one must work against combustion, the most thermodynamically favorable reaction. The ability to produce only one desired product among many possibilities is also required. We are studying the relationship between surface atomic arrangements of an oxide with the catalytic properties. Single crystals of ZnO were used, which may expose surfaces that have zinc ions more outwardly positioned than oxygen ions, or vice versa. The rates of alcohol decomposition reactions on the two different types of surfaces are found to be different. We are also studying mixed oxides of vanadium oxides in the selective oxidation of butane and propane. Magnesium orthovanadate is a rather selective catalyst for the oxidative dehydrogenation of alkanes, which contrasts the selective oxidation to oxygenates (propionic acid or maleic anhydride) on the vanadyl orthophosphate catalysts. Experiments are under way to identify factors that determine dehydrogenation vs. oxygenate formation in this alkane oxidation on vanadium oxide-based catalysts.

309. *Supported f-Element Organometallic Complexes: Surface Chemistry and Catalysis*

T.J. Marks, R.L. Burwell, Jr. **$88,000**
Department of Chemistry

The project objective is to elucidate, via a coordinated chemical and spectroscopic investigation, the nature of species produced when organo-f-element complexes (and by inference, early transition metal complexes) are adsorbed on high-surface-area metal oxides. These species constitute some of the most active olefin hydrogenation catalysts yet discovered and are also highly active for ethylene polymerization. Catalytic hydrogenation studies have now expanded from initial Cp'_2MR_2/propylene systems ($Cp' = (CH_3)_5C_5$, M = Th,U) to other olefins (for Cp'_2MR_2 catalysts, N_t: propylene $\simeq$ 1-butene $\gg$ isobutylene), metal complexes (N_t: $Cp'MR_3 \gg Cp'_2MR_2 > Me_2Si[(CH_3)_4C_5]_2MR_2 \gg Cp_3MR$), and supports (for Cp_2MR_2 catalysts, N_t:dehydroxylated Al_2O_3 > partially dehydroxylated Al_2O_3 $\gg$ dehydroxylated SiO_2). Mechanistic studies have included deuterium labeling, CO poisoning, and detailed kinetic and activated parameter measurements. A number of other complexes, catalytic reactions, and supports are also under examination. Closely integrated with this effort are high-resolution CPMAS ^{13}C NMR studies of the adsorbed molecules. Using isotopic labeling, differing magnetic fields, and various pulse techniques, it is possible to obtain significant adsorbate structural and dynamic information at less than monolayer coverages. It is also possible to monitor reactions *in situ*. We have demonstrated the applicability of this technique to elucidating metal carbonyl surface chemistry.

310. *Chemical Interactions in Multimetal–Zeolite Catalysts*

W.M.H. Sachtler **$117,900**
Department of Chemistry

Catalysts that contain a reduced transition metal inside the cavities of a zeolite possess a high industrial potential. The zeolite structure can be exploited for stereospecific reactions, and strong acid sites can be formed, permitting bifunctional catalysis. Potential problems are the low reducibility of some metals and their high mobility, leading to loss of dispersion. To solve these problems we have studied the genesis and growth of metal particles inside the cavities of Y zeolites, and their catalytic performance. The following results were found: (1) The reducibility of nickel could be increased from 42 to 93% by preventing the migration of unreduced nickel ions into small zeolite cavities. This was achieved by filling these cavities with chromium or manganese ions. (2) Platinum ions tend to migrate into sodalite cages, but if calcination is carried out at 300°C, the ions remain in the supercages, and virtually 100% dispersion can be achieved. (3) Reduced transition metals can be "anchored" to the zeolite by unreduced ions such as iron or chromium, which leads to a dramatic increase in dispersion maintenance under severe conditions. This anchoring model has been verified by EXAFS of Rh–Cr/NaY. (4) Pt/NaY catalysts catalyze the ring opening of methylcyclopentane with different selectivity than Pt/SiO_2; this is rationalized on stereochemical grounds.

311. Structure and Chemistry of the Interaction of Organometallics with Surfaces

D.F. Shriver **$143,700**
Department of Chemistry **(18 mo.)**

One objective of this research is to characterize organometallics attached to surfaces, to elucidate the cluster–support interaction. Parallel model studies of organometallic compounds in solution and of conventionally prepared heterogeneous catalysts are performed to obtain a coherent picture of fundamental organometallic chemistry related to CO activation by heterogeneous catalysts. Based on our previous experience with the chemistry of CO in homogeneous solution chemistry, we have postulated that electropositive metals promote CO cleavage and migration insertion reactions. Therefore, we are studying supported mixed-metal clusters that contain one electropositive metal (e.g., Rh–Fe clusters on metal oxide surfaces by infrared and EXAFS techniques). The catalytic chemistry of these same materials is under investigation.

University of Pennsylvania
Philadelphia, Pennsylvania 19104

312. Desorption and Reaction Kinetics Studied on Model Supported Catalysts

R.J. Gorte **$78,900**
Department of Chemical Engineering

Temperature programmed desorption (TPD) and reaction studies are being carried out on model catalysts in which small particles of a metal (platinum, rhodium, or palladium) are deposited on top of an oxide, or a thin film of oxide is deposited on top of a metal. For metals on oxides, the particle size is characterized from adsorption coverages of CO or H_2. The catalytic properties of these samples, including adsorption properties and reaction rates for ethane hydrogenolysis, are then measured as a function of particle size and oxide composition. For small metal particles, initial results indicate that the distribution of crystal planes on the particles are affected by the substrate composition and the particle size. For oxides on metals, results indicate that some oxides tend to "wet" the metal surface while others form clusters.

313. Synthesis and Properties of New Preceramic Materials

L.G. Sneddon **$150,000**
Department of Chemistry

This project is concerned with establishing new, high-yield, selective procedures for the synthesis of heteronuclear ring and cluster compounds containing the element boron, in conjunction with nitrogen, phosphorous, or carbon. The synthetic approach focuses on developing new transition-metal catalysts, analogous to those now widely employed in organic chemistry, to activate boron–hydrogen bonds for dehydrocoupling, ring expansion, substitution reactions, and so forth. Particular emphasis is on the production and chemical and physical properties of new molecular and polymeric compounds that may serve as precursors to important solid-state materials (e.g., boron nitride, boron phosphide, and boron carbide).

314. Catalytic Hydrogenation of Carbon Monoxide

B.B. Wayland **$107,500**
Department of Chemistry

The project objective is to learn how to use the unique properties of rhodium porphyrins in achieving catalytic hydrogenation of carbon monoxide at mild conditions. Rhodium porphyrins react with H_2 and CO at pressures less than one atmosphere to produce a metalloformyl complex that is a primary intermediate in the hydrogenation of CO. Several catalytic schemes are proposed that take advantage of the unique reactivity of rhodium porphyrins coupled with the aldehyde-like character of the metalloformyl intermediate. Multifunctional catalysts that use rhodium porphyrins and a second catalyst known to promote the hydrogenation of aldehydes are particularly promising candidates for achieving low-pressure hydrogenation of CO. Solvent effects are explored as one means of tuning the thermodynamic and kinetic parameters for optimum catalytic behavior. Results from studies of the rhodium porphyrin system provide a guide in designing new materials that retain the favorable thermodynamic factors, but have improved reaction kinetics. Comparative studies using variation of the ligand array and central metal (cobalt, rhodium, iridium) are used to optimize the desired catalyst behavior.

Pennsylvania State University
University Park, Pennsylvania 16802

315. Mechanistic Studies of Carbon Monoxide Reduction

G.L. Geoffroy **$116,000**
Department of Chemistry

The reactivity of methylene, ketene, and imido ligands on metal clusters is being explored. The ketene ligands on triosmium clusters have been converted into enolate, vinyl, and acetyl ligands by reactions with electrophiles and nucleophiles. Current focus is on further developing the synthetic chemistry of such coordinated ketene ligands. The coupling of imido ligands on clusters with carbenes, acyls, methoxycarbonyl, and alkyne ligands has been observed to give a variety of organic and organometallic products, including imines, maleimides, and pyridinones. Recent work has shown that halides promote the carbonylation of imido ligands to form isocyanates and also promote the formation of imido ligands from nitroso reagents. The mechanisms of these latter transformations are currently under study.

316. *Determination of the Distribution of Hydrogen in Coal by FTIR*

P.C. Painter **$94,000**
Department of Materials Science and Engineering

The project objective is to measure the distribution of hydrogen in coal according to functional group, which will provide considerable insight into coal structure, particularly for those coals for which ^{13}C NMR values of the fraction aromatic carbon content are also available. Fourier transform infrared spectroscopy (FTIR) is the principal tool used in this investigation. Although this technique has been applied to coal characterization for a number of years, results reported by various groups differ considerably. Accordingly, a major part of the initial research focuses on determining the precision of the numbers that can be obtained.

317. *Transition Metal Catalyzed Transformations of Unsaturated Molecules*

A. Sen **$117,000**
Department of Chemistry **(16 mo.)**

The homogeneous catalysis of organic transformations by transition metal compounds is of considerable practical and scientific importance because of the high efficiency, high specificity, and low energy demands often associated with such systems. The project objectives are: (1) to achieve a fundamental mechanistic understanding of a number of important homogeneous catalytic systems and (2) to use this knowledge to develop new and useful catalytic processes. Catalytic systems under study are: (1) palladium(II)- and rhodium(I)-catalyzed copolymerization and cooligomerization of carbon monoxide with olefins that lead to the formation of unique polyketones with strictly alternating structures; (2) a palladium(II)-catalyzed "double carbonylation" reaction that converts organic halides into molecules with vicinal diketo groups; and (3) palladium(II)-catalyzed isomerization of carboxylic acid chlorides that allows accurate determination of the relative free energies of formation of isomeric acid chlorides and, by extrapolation, other isomeric alkyl derivatives. For the first system, our studies have led to a detailed understanding of the unique chain-growth mechanism for the polymer formation. Through the study of model compounds, we have also elucidated the mechanistic steps involved in the latter two catalytic systems.

318. *Characterization of Catalysts with Metal-Support Effects and of the Species Adsorbed on Their Surfaces*

M.A. Vannice **$104,800**
Department of Chemical Engineering

The project objective is to elucidate the chemistry involved in the creation of metal–support interactions that have pronounced effects on adsorption and catalytic behavior. Focus is on characterizing adsorbed molecules, and the chemical and physical state of the metal and support. The project involves a study of heats of adsorption for H_2, CO, and O_2 on platinum, palladium, and nickel using a modified differential scanning calorimeter combined with a thermal gravimetric analysis unit and separate chemisorption experiments. Kinetic investigations are being made on hydrogenation reactions involving aromatic hydrocarbons and the C–O bond in carbon monoxide, acetone, and crotonaldehyde. Scanning transmission electron microscopy will be used to better define the state of the metal particles and the particle size distributions. Solid-state magic angle spinning NMR will be used to study adsorbed ^{13}C-labeled CO and hydrocarbons and to conduct Knight shift experiments on the metal itself (^{195}Pt), to determine the influence of the support on conduction electrons. This multifaceted approach attempts to explain the much higher catalytic activities found for CO hydrogenation and for the 100-fold enhancements just found for acetone hydrogenation over TiO_2-supported platinum. The applicability of a recently proposed model invoking special active sites created at the metal–support interface is being carefully examined. Heats of adsorption of H_2, CO, and O_2 on palladium exhibit a similar pattern: they all increase significantly as the palladium crystallite size decreases below 3 nm, and the support has little effect. A similar dependence on crystallite size does not appear to occur for these gases on platinum, but the support (such as TiO_2) can noticeably decrease CO heats of adsorption on platinum.

University of Pittsburgh
Pittsburgh, Pennsylvania 15260

319. *Studies of the Fundamental Nature of Catalytic Acidity, Sites, and Intermediates*

W.K. Hall **$90,000**
Department of Chemistry

Recent research on H-zeolites has yielded results characteristic of reactions in superacids, and has led to the suggestion that secondary and tertiary alkylcarbonium (carbenium) ions are stabilized within these materials. Both physical (MASNMR and ESCA) and chemical means will be used to test this hypothesis. Known stable carbonium ions will be used as reference standards, and the interaction of alcohols and olefins with the Bronsted sites will be investigated. The research will apply to the reactivity of the Bronsted acid sites and the nature of the intermediates formed; the latter will control the selectivity in product formation. The properties of carbonium ions on zeolite surfaces will be characterized for the first time by MASNMR and by ESCA, and related to those in superacids, as described in the literature.

320. *Studies of Supported Metal Catalysts*

D.M. Hercules **$125,330**
Department of Chemistry **(16 mo.)**

We have investigated the effect of additives on the early stages of catalyst preparation (i.e., impregnation), by examining the effect of additives on the isoelectric point (IEP) of the alumina support and the ensuing impact on the adsorption of metal complexes from solution. We have examined the influence of additives known to promote the HDS reaction (boron, titanium) on the state and dispersion of Mo/Al_2O_3 and Co/Al_2O_3 catalysts. A method has been developed to use ESCA to determine the speciation of oxidic alumina-supported metal catalysts, and has been used to study the speciation of Co/Al_2O_3 catalysts. The results were consistent with published cobalt speciation data derived from Mossbauer spectroscopy. Laser Raman spectroscopy (LRS) was used to identify and quantitate the species present in CoMo/TiO catalysts, which cannot be readily quantified by other analytical techniques.

321. *Infrared Studies of Influence of Alkali Metals on C–O Bond in Chemisorbed Carbon Monoxide*

J.T. Yates, Jr. **\$152,500**
Department of Chemistry

This research project is designed to probe the interaction of adsorbed alkali metals and electronegative poisons with adsorbed carbon monoxide on transition metal single-crystal surfaces. Information obtained by reflection infrared spectroscopy, x-ray, photoelectron spectroscopy, and temperature-programmed desorption will yield models of the interaction, and a deeper understanding of the alkali promotion effects and electronegative poisoning effects observed in catalytic chemistry on transition metals. Recently, the range of S poisoning on a nickel(111) single crystal has been determined, and the nature of K···CO interactions has been probed in detail. A mixture of short- and long-range effects is observed.

Purdue University
West Lafayette, Indiana 47907

322. *Reduction of Aromatic Compounds Derived from Coal by Calcium*

R.A. Benkeser **\$65,000**
Department of Chemistry

Previously we have shown that calcium dissolved in ethylenediamine is very effective in reducing aromatic ring systems to cyclic monoalkenes (tetra hydro products). When these same reductions are carried out in a solvent system of ethylenediamine and an alcohol, the reaction stops at a dihydro stage, thereby resembling the well-known Birch reduction. The scope of the calcium–amine reducing system has now been broadened to include aromatic carboxylic acids. For example, 2-methylbenzoic acid can be reduced to 2-methyl-1,4-dihydrobenzoic acid (95% yield), 3-methylbenzoic acid to 3-methyl-1,4-dihydrobenzoic acid (92%), and 4-methylbenzoic acid to 4-methyl-1,4-dihydrobenzoic acid (94%). Many of the other isomeric dimethylbenzoic acids are reduced with equal ease to their corresponding 1,4-dihydro products. While similar reduction products can be obtained by using sodium or lithium in liquid ammonia, the calcium–amine procedure is preferable in large-scale reductions where costs and safety become significant factors. It has also been shown that the calcium salt of some of the aforementioned acids can be reduced with equal ease to the same 1,4-dihydro products obtained by reducing the acid itself. This clearly indicates that the ethylenediamine solvent can function as the sole proton source in such reductions.

Rensselaer Polytechnic Institute
Troy, New York 12180

323. *Selective Transformations of Carbonyl Ligands to Organic Molecules*

A.R. Cutler **\$105,000**
Department of Chemistry

The Rh(I) catalyzed hydrosilylation of metal acyl complexes M-COR [M = Cp(CO)(L)Fe and Ru, $(CO)_5MN$] to α-silyloxyalkyl derivatives M-CH($OSiHR_2'$)R [R′ = Et, Ph] has been investigated. Novel carbonylation reactions using η^5 / η^3-Indenyl (In) Fe complexes efficiently generate Fe acyl complexes under mild conditions. Fully characterized $(\eta^3\text{-In})Fe(CO)_3^-$ (In ring fold angle 21°) reacts with MeI and gives $(\eta^5\text{-In})(CO)_2Fe\text{-}COCH_3$, for example. Treatment of $(\eta^5\text{-In})(CO)_2Fe\text{-}R$ with η^5-Cp or $\text{-InFe}(CO)_2^-$ affords bimetallic terminal acyl compounds $In(CO)Fe(\mu\text{-}CO)_2Fe(In\ or\ Cp)(COR)^-$, which degrade (1 atm CO) to $In(CO)_2FeCOR$ [R = CH_3, CH_2OMe]. This bimetallic reaction chemistry was used in adding two CO and converting $In(CO)_2FeCH_3$ into $In(CO)_2Fe\text{-}COCH(OEt)CH_3$. Anionic, phosphide-substituted compounds $Cp(CO)(PPh_2)Fe\text{-}R^-$ [R = CH_3, $COCH_3$], thus far, have been prepared (by deprotonating their PPh_2H precursors), and their electrophile-promoted CO insertion–deinsertion reactions are being studied. The extremely reactive 16-electron Lewis acid $Cp(CO)(\eta^2\text{-}CH_3CH{=}CH_2)Fe^+BF_4^-$, prepared by protonating the η^3-allyl complex, has been characterized (e.g., ^{11}B and ^{19}F NMR spectroscopy) at -70°C. This Lewis acid and its derivatives $Cp(CO)Fe(CH_3CN)_2^+$ and $Cp(CO)Fe(CH_3CN)(THF)^+$ serve as useful synthetic intermediates in preparing examples of $Cp(CO)Fe(L)(L')^+$. These organoiron Lewis acids did not convert $Cp(CO)_3Mo\text{-}R$ into heterobimetallic μ-(η^2-C,O) acyl complexes $Cp(CO)_2Mo(\mu\text{-}OCR)Fe(CO)Cp^+$ [R = H, CH_3].

University of Rochester
Rochester, New York 14627

324. *Transition Metal Activation and Functionalization of Carbon–Hydrogen Bonds*

W.D. Jones **\$143,000**
Department of Chemistry **(18 mo.)**

This project focuses on (1) the continued investigation of the fundamental thermodynamic and kinetic factors that influence carbon–hydrogen bond activation at homogeneous transition metal centers; and (2) the conversion of hydrocarbons into functionalized products of potential use to the chemical industry. Our goals are (1) to identify new transition metal complexes capable of activating arene and alkane C–H bonds, (2) to quantitatively evaluate the kinetic and thermodynamic stability of these complexes, and (3) to examine routes for functionalization of the activated hydrocarbons. These studies will also contribute to the formulation of a unified theory of C–H bond activation that applies to other transition metal complexes. The specific complexes involved in these studies are derivatives of the formulation $(C_5Me_5)Rh(PR_3)(R)H$, $Fe(PMe_3)_2(CNR)_3$, $Ru(PR_3)_4(R)H$, and $Rh(CNR)_3H$. Functionalization will focus on isocyanide and acetylene insertion reactions. New compounds that activate hydrocarbon C–H bonds include $HRe(PR_3)_5$, $HRe(PR_3)_2(CNR)_3$, $CpRe(PR_3)H_4$, $CpRe(PR_3)_2H_2$, and $(\eta^6\text{-}C_6H_6)Re(PPh_3)_2H$.

University of South Carolina
Columbia, South Carolina 29208

325. *Ligand Transformations and Catalysis by Transition Metal Cluster Compounds Containing Sulfur*

R.D. Adams **\$92,760**
Department of Chemistry

Sulfur contamination is a major problem in the use of transition metal catalysts for fuel conversion processes. The project objectives are (1) to study the structure, bonding, and reactivity of carbon and small hydrocarbyl ligands with sulfur in transition metal cluster compounds; and (2) to investigate the potential of these compounds to produce small molecule transformations catalytically. These studies will help to reveal the nature of sulfur–ligand interactions and their reactivity at multinuclear metal sites. It is believed that the development of catalysts containing sulfur will help to reduce, if not eliminate, the adverse effects produced by sulfur on nonsulfur-containing catalysts. Preliminary results strongly support these contentions.

SRI International
Menlo Park, California 94025

326. *High-Temperature Chemistry of Complex Vaporization-Decomposition Processes*

D.L. Hildenbrand, **$71,830**
R.D. Brittain, K.H. Lau
Physical Sciences Division

The project objective is to obtain fundamental thermodynamic data for a variety of high-temperature vaporization-decomposition processes that are relevant to current and emerging energy technologies, such as stack gas cleanup, coal gasification, hydrogen generation, and MHD. These processes are being studied by high-temperature mass spectrometry and the torsion-effusion method so that both vapor composition and absolute pressures are determined. For substances that simultaneously undergo both decomposition and direct vaporization, particular emphasis is on quantitative determination of the relative contributions from each process, and on thermochemical characterization of the complex vapor species. Current studies are concerned with the alkali chromates and molybdates. These alkali salts are especially interesting in that vaporization occurs mainly via stable gaseous metal chromate and molybdate molecules, about which little is known. Special effort is devoted to obtaining accurate vapor entropies that can be checked for compatibility with known and estimated molecular constants, particularly the low-frequency alkali–oxygen vibrations associated with the unusual polytopic bonding in these species.

327. *Interaction of Carbon and Sulfur on Metal Catalysts*

J.G. McCarty **$80,000**
Materials Research Laboratory

Carbon deposition and sulfur poisoning present difficulties for a majority of the catalytic processes involved in energy conversion technologies. Chemisorbed carbon and hydrocarbon fragments and amorphous carbon deposits occupy the working surfaces of the catalyst in applications such as hydrocarbon reforming, hydrotreating, hydrocarbon steam reforming, and hydrocarbon synthesis under typical commercial conditions. At high levels, chemisorbed sulfur generally deactivates metal catalysts, but at low levels, adsorbed sulfur has a more subtle effect on the activity and selectivity of a catalyst. This project focuses on the effect of chemisorbed sulfur on the thermodynamics and reactivity of surface carbon for both dispersed and well-characterized metallic catalysts of commercial interest. In studies with dispersed catalysts, fused iron and alumina-supported platinum surfaces will be uniformly treated and locally equilibrated with low- and high-levels of chemisorbed sulfur. Thermodynamics of carbon deposition, structure and morphology of deposited carbon, and hydrogasification rates will be examined as functions of temperature and sulfur coverage using equilibrium gas recirculation, Fourier transform infrared spectroscopy (FTIR) and electron microscopy, and temperature programming techniques, respectively. In studies with well-characterized polycrystalline iron and single-crystal platinum surfaces, the effect of chemisorbed sulfur on carbon surface segregation thermodynamics, two-dimensional long-range order, and the nature of surface bonding will be determined by Auger electron spectroscopy (AES) and surface analysis by laser ionization (SALI), low-energy electron diffraction (LEED), and thermal desorption techniques, respectively.

Stanford University
Stanford, California 94305

328. *Catalytic Steam Gasification of Carbon*

M. Boudart **$120,000**
Department of Chemical Engineering **(17 mo.)**

Extensive investigations of the last decade have improved understanding of the bonding and the electronic properties of transition metal carbides. The temperature-programmed reaction between MoO_3 or WO_3 with NH_3 provides a new way to prepare Mo_2N and W_2N powders with specific surface areas as high as 220 and 100 m^2g^{-1}, respectively. Temperature-programmed carburization of Mo_2N and W_2N powders in CH_4–H_2 mixtures leads to metastable face-centered cubic carbide phases. The high specific surface area of Mo_2C or W_2C, based on the BET method or methods recommended for assessing the specific surface area of microporous materials, is higher than ever previously reported. In discussing the fundamental work on new catalytic materials, several reactions were investigated to compare the catalytic activity and specificity of these high-surface-area carbides to platinum-group metals. These studies include the isomerization and hydrogenolysis of neopentane and the reactions of H_2–O_2 and N_2O–H_2. Hydrogenolysis of neopentane occurs on tungsten carbide, whereas the isomerization of neopentane occurs only when the carbide is previously exposed to dioxygen. The value of the turnover rates for the reactions between H_2–O_2 or H_2–N_2O on tungsten carbide has been shown to be an order of magnitude less than that for platinum.

329. *Molecular Beam Studies of the Dynamics and Kinetics of Heterogeneous Reactions on Single-Crystal Surfaces*

R.J. Madix **$122,000**
Department of Chemical Engineering

The probability of C–H bond activation of linear alkanes upon collision with an Ir(110) surface has been determined using molecular beam techniques. This surface exhibits a unique ability for low-temperature cleavage of C–H bonds of alkanes (adsorbed on the surface) of molecular weight higher than ethane. We have clarified the role of this reaction channel in collisional activation and discovered a second channel operative at high kinetic energies of the incident molecules. At surface temperatures above about 500 K and molecular kinetic energies between 10 and 50 kJ/mol, the alkanes show reaction probabilities at the surface that increase with molecular weight and are invariant with kinetic energy. Methane shows no reactivity in this energy range, and ethane shows a reaction probability of 0.03. Ethane could not be activated by low-temperature adsorption in previous studies. Butane, with a reaction probability of 0.2, is the most reactive. The activation probability can be increased by lowering the surface temperature or the kinetic energy, consistent with the role of trapping in producing reaction at temperatures near the desorption temperatures of the respective alkanes. Reaction probabilities of butane can be increased to 0.7 at 100 K and 2 kJ/mol. At a given surface temperature the activation of alkanes present in the gas phase with a Boltzmann distribution of velocities proceeds via trapping at the very lowest kinetic energies and by a direct process at intermediate kinetic energies. Focus is on Boltzmann distribution up to translational energies of about 120 kJ/mol. At energies above about 80 kJ/mol, a direct, activated process causes the reaction probability to increase. The rate of increase with translational energy decreases with molecular weight. This may be due to dissipative channels in the collision that drain energy from the reaction coordinate. Translational to rotational energy conversion may also contribute to dissipation of the reaction energy.

Syracuse University
Syracuse, New York 13244

330. *Metal–Support Interactions: The Effect of Catalyst Preparation on Catalytic Activity*

J.A. Schwarz **$95,000**
Department of Chemical Engineering and Materials Science

This research is systematically examining the effect of preparation procedures, including metal concentration and pH of the impregnation solution, on the catalytic properties and the chemical structures of supported-metal catalysts. Design parameters have been identified for Ni/Al_2O_3 catalysts prepared by incipient wetness and wet impregnation from nickel nitrate solution in contact with a γ-Al_2O_3 support. The metal dispersion, activity for C_1, C_2, and C_3 formation under synthesis conditions, and the carbon deposited during reaction appear to be predictable based solely on the properties of the electrolytes from which these catalysts were formed. ESCA results have clearly identified that $NiAl_2O_4$ is the only catalytic species on low-weight-loading catalysts, and Ni and $NiAl_2O_4$ comprise the architectural arrangement of nickel speciation for high-weight-loading catalysts. The rate of methanation over catalysts containing only $NiAl_2O_4$ on the surface is controlled by the rate of $CO_{(s)}$ dissociation. High-weight-loading catalysts prepared by incipient wetness consist of particle-like nickel; the rate of methanation over these catalysts is controlled by the rate of hydrogenation of CH_x.

University of Texas
Austin, Texas 78712

331. *Study of Synthesis Gas Conversion over Metal Oxides*

J.G. Ekerdt **$62,000**
Department of Chemical Engineering

The goals of this project are (1) identification of the reaction intermediates present during CO hydrogenation reactions, (2) determination of the reaction pathways whereby the intermediates are converted into products, and (3) development of an understanding of the causes for catalytic activity and selectivity to C_{2+} products. Direct CO hydrogenation into branched hydrocarbons, isosynthesis, and into low-weight alcohols is investigated over zirconium dioxide-based catalysts. Experiments are conducted at 35 atm and at atmospheric pressure. Oxygen and carbon isotope-labeling studies and reaction-rate studies at both pressures have revealed the reactions that occur during chain growth and termination, and during the activation of CO to the intermediates needed in chain growth. The studies also suggest the configuration of the active site at the zirconium dioxide surface. The effect of alkali additives on the concentration of active sites and on the rate of termination to branched products, and how catalyst synthesis conditions affect the concentration of the sites for CO activation are currently under investigation.

332. *Morphological Aspects of Surface Reactions*

J.M. White **$115,000**
Department of Chemistry

An integrated research project combining reaction rate, surface spectroscopy, and surface microscopy will be conducted on rhodium-based catalysts including atomically dispersed, small clusters and thin films supported on oxides and bulk single crystals. Reactions under investigation include H_2–D_2 exchange, carbon monoxide oxidation, and hydrogenation of ethylene. Rate measurements will be made from pressures as low as 10^{-6} to 760 torr and at temperatures below 350 K. Detailed surface analysis will be made using thermal desorption spectroscopy, secondary ion mass spectrometry, vibrational spectroscopy, and photoemission. Electron microscopy will be performed to provide particle size and morphology. The sample environments will be carefully controlled and evaluated, particularly during transfers between various instruments. The combination of this data on a series of closely controlled samples will provide for direct correlations between particle morphology and catalytic activity over a broad range of conditions.

Texas A and M University
College Station, Texas 77843-3255

333. *Catalysts and Mechanisms in Synthesis Reactions*

J.H. Lunsford **$88,100**
Department of Chemistry

The objective of this research is to understand the surface generation of gas-phase radicals and the importance of these radicals in catalytic processes. A matrix isolation system in tandem with a hot catalyst bed is used to trap the radicals, which are subsequently analyzed by EPR spectroscopy. Recent studies have provided insight into the C–H activation of methane and the mechanism by which the oxidative coupling occurs. Quantitative comparison of the radical flux from the surface with the overall rate of ethane and ethylene formation supports gas-phase methyl radical coupling as a primary pathway for the formation of dimerization products. The catalytic production of gas-phase methyl radicals over the lanthanide oxide series also has been determined and compared with methane conversion in a conventional flow reactor. In general, the catalysts effective in generating gas-phase methyl radicals (La_2O_3, Nd_2O_3, and Sm_2O_3) are also good catalysts for the selective oxidation of methane. Using the same matrix isolation system, it has been shown that bismuth oxide is capable of generating gas-phase 1-methylallyl and 2-methylallyl radicals from 1-butene and isobutylene, respectively. These results, together with those previously obtained on other alkanes and alkenes, suggest that factors such as availability of abstractable hydrogen and stereochemistry may be equally as important as C–H bond strength in determining the rate of radical formation.

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

M.P. Rosynek **\$79,100**
Department of Chemistry

This project is an investigation of the influence exerted by lanthanide oxide support materials on the catalytic and surface properties of dispersed transition metals. Studies have focused primarily on catalyst preparation and characterization, with particular emphasis on the application of temperature-programmed reduction (TPR) techniques. We have examined the reduction behaviors of dispersed cobalt, nickel, and rhodium catalysts prepared from chloride, nitrate, acetate, and chloramine precursors. Using a combination of TPR/MS and XPS techniques, we have demonstrated that both the mechanism of the reduction process and the nature of the resulting surface for cobalt catalysts supported on SiO_2, TiO_2, CeO_2, La_2O_3, and Eu_2O_3 are strongly dependent on whether a preoxidation step is employed in the pretreatment sequence. Direct reduction in H_2 of supported $Co(NO_3)_2$ results in a catalyst containing surface regions of virtually irreducible Co(II), while preoxidation of the nitrate to Co_3O_4 prior to H_2 treatment facilitates complete reduction to metallic cobalt. The TPR method has also revealed that rhodium salts are considerably more difficult to reduce when dispersed on basic oxides such as La_2O_3 and Eu_2O_3 than on neutral materials such as SiO_2.

University of Utah
Salt Lake City, Utah 84112-1183

335. *Ligand Intermediates in Metal-Catalyzed CO Reduction*

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

The basic goals of this project are the synthesis and study of homogeneous complexes containing ligand types (-CHO, =CHOH, $-CH_2OH$, ≡C, $=CH_2$, $H_2C=O$, -OCHO, CO_2, and so forth) believed to be intermediate in the metal-catalyzed conversion of CO/H_2 and CO_2/H_2 gas mixtures to organic molecules. We are seeking mechanistic understanding of the steps involved in catalytic CO and CO_2 reduction, and insight needed for the design of new catalysts. This year we have focused on characterizing reactions that proceed by odd-electron intermediates. We find that hydride abstraction from benzyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ by Ph_3C^+ PF_6^- gives benzylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]^+$ PF_6^- with a K_H/K_D of 5.4 under N_2, but only 1.0 under air (O_2). Coupled with electrochemical data, this establishes that hydride abstraction proceeds via initial electron transfer. We also find that the chemical or electrochemical oxidation of methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)\text{–}(PPh_3)(CH_3)$ gives methane and (complexed) ethylene in good yield. This suggests a possible path for controlled methane oxidation; the mechanism is under intense study. We are also studying the formation and reactions of the coordinatively unsaturated species $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$, which can be generated by reductive elimination of RX (a key step in many types of catalysis) from a variety of easily generated $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(R)(X)]^+$ (R=alkyl, H; X = H, halide) complexes.

336. *Carbon-13 NMR of Solid-State Hydrocarbons and Related Substances*

D.M. Grant, R.J. Pugmire **\$100,770**
Department of Chemistry

Work on solid-state nuclear magnetic resonance (NMR) methods of single-crystal and magic angle spinning (MAS) involves model compounds to be used for calibration and standardization of spectra of coals, coal macerals, and related materials. Current work on single crystals provides a better understanding of shielding anisotropies and the orientational features of the important dipolar dephasing experiment. Rotation of a single crystal is required to obtain information on chemical shift anisotropy. A mechanical flipper probe has been demonstrated and is under further development for obtaining these spatially required correlation data. The flipper probe allows a two-dimensional method to be used, which has the capacity of indexing 5 to 10 times the number of peaks done by traditional approaches. The single-crystal probe allows us to obtain the shielding anisotropies in fused aromatics where it has been found that the internal bridgeheads can be distinguished on the basis of shielding anisotropies from the peripheral carbons. The relative amounts of protonated aromatic carbons and internal bridgeheads impact combustion rates of such hydrocarbons. Initial results show relaxation anisotropy can be studied in single crystals. Both the dipolar dephasing rate and relaxation anisotropy depend on the orientation of C–H bonds. An ultra-high-speed (0 to 8,000 r.p.s.) rotor for MAS work has been developed. The higher rotation rates allow use of our 4.7 tesla magnet instead of the 2.35 tesla systems used previously. Reduced rotor diameters also allow for significant increases in the RF fields at reduced power dissipation and improved cross-polarization (CP) efficiencies. Using variable angle spinning has provided a method for obtaining shielding tensors from multicrystalline powders.

337. *Comprehensive Characterization Studies of Sulfided Molybdena Catalysts*

F.E. Massoth **\$117,000**
Department of Fuels Engineering **(18 mo.)**

Catalysts containing molybdenum supported on various aluminas were found to have a strong attachment of the molybdenum-oxide phase to the alumina surface, resulting in monomolecular dispersion of the molybdenum over the alumina surface, provided the monolayer capacity of the alumina is not exceeded. In the latter case, multilayers and sometimes bulk MoO_3 are present. During sulfiding, the molybdenum-oxide phase breaks up into smaller monolayer MoS_2 slabs covering less alumina surface, while multilayer oxide catalysts result in multilayer MoS_2 clusters of larger size. The relative size of the MoS_2 (from NO chemisorption) was found to vary appreciably with the particular alumina support used. However, for a given alumina support, the same size MoS_2 slabs are found independent of the molybdenum content. Catalyst activities for hydrodesulfurization, hydrogenation of aromatics, and C–N hydrogenolysis were found to roughly correlate with NO chemisorption. Sufficient deviations were obtained to demonstrate that the NO adsorption sites and catalytically active sites are not directly related. Results indicate that different types of active sites are involved in the three aforementioned reactions. To increase catalytic activity, catalysts with small MoS_2 sizes and higher surface coverages should be developed.

Wayne State University
Detroit, Michigan 48202

338. Surface Composition–Reactivity Relationships in Heterogeneous Catalysis
A. Brenner **$95,000**
Department of Chemistry

Research focuses on catalysts of base metals. (1) Information on the change of oxidation state with the temperature of catalyst activation is needed to improve catalyst syntheses. Temperature-programmed reduction and oxidation studies have been extended to include the bulk compounds Co, CoO, Co_3O_4, H_2OsCl_6, V_2O_5, ThO_2, Rh_2O_3, Mn_2O_3, H_2PtCl_6, and IrO_2. Temperature requirements for reduction vary greatly, and during reoxidation some of the compounds form intermediate oxides, which decompose at higher temperatures. (2) Fe_2O_3 is a high-spin d^5 compound that appears to have no activity for H_2–D_2 exchange. This was used to support the electronic theory of catalysis. We find that the activity of Fe_2O_3 strongly depends on pretreatment and can be highly active for the exchange reaction. (3) There is currently no technique available for measuring the surface area of Mo(0) in catalysts. Thus we studied the chemisorption of H_2, O_2, CO, NO, and C_2H_4 on Mo and MoO_2. All gases adsorbed on the samples, but only O_2 gave quantitative results (one O atom per surface Mo atom) and only H_2 significantly discriminated between the two compounds. (4) We continue to investigate the activity of Mo (unsupported), Mo/Al_2O_3, and Mo/SiO_2 for H_2–D_2 exchange; the rate of reaction should be slow if the Mo can be atomically dispersed. The activity per site is high and similar for the three forms of Mo. (5) Ethylene deuterogenation is studied. It is expected that isolated sites would yield $C_2D_2H_4$; but $C_2D_nH_{6-n}$, $n = 0$, 1 to 6 would result on a metal crystallite. Results show that $Mo(CO)_3/Al_2O_3$ gives mainly $C_2D_2H_4$, but sintering of this material at elevated temperatures substantially increases the amount of isotopic scrambling.

University of Wisconsin
Madison, Wisconsin 53706

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

The organometallic chemistry of bimetallic compounds will be investigated (1) to discover new heterobimetallic compounds that can serve as catalysts for CO hydrogenation and (2) to obtain a better understanding of the chemistry of bridging hydrocarbon ligands bonded to multiple metal centers. Heterobimetallic compounds in which the metals are linked by a heterodifunctional ligand and by a metal–metal bond will be synthesized. A search will be made for such compounds that will react with H_2 to produce heterobimetallic dihydrides. The oxidative addition of metal dihydrides to a second metal center will be explored as a route to heterobimetallic dihydrides. Bimetallic compounds with one early and one late transition metal will be investigated since the resulting dihydrides are expected to have one hydridic and one acidic metal–hydrogen bond, and may act as powerful reducing agents for polar molecules such as CO. The chemistry of newly discovered bridging methylidyne complexes will be studied as models for surface-bound CH units. The synthesis and reactions of bimetallic compounds with a bridging methylene and terminal methyl group will be studied as models for the carbon–carbon bond-forming process in the Fischer-Tropsch reaction.

340. Acid Sites Formed by Doping Cations onto Oxide Surfaces: Theoretical Aspects and Experimental Studies
J.A. Dumesic **$85,000**
Department of Chemical Engineering

During the past year our research has focused on the acidic and catalytic properties of silica-supported metal oxides. These studies have used pyridine adsorption to determine gravimetrically the number of acid sites, to probe microcalorimetrically the acid strength, and to determine using infrared spectroscopy the nature of the acid sites (i.e., Lewis vs. Bronsted acidity). Essentially all cations studied displayed Lewis acidity when supported on silica; however, the acid strength appears to correlate with the electronegativity of the oxide. Cations such as Sc^{3+} and Mg^{2+} with low electronegativity were weaker Lewis acids than cations with higher electronegativity such as Al^{3+} and Ga^{3+}. In contrast, relatively few oxides on silica generated Bronsted acidity, even after exposure to water. One special case where Bronsted acidity is generated in a manner similar to that for zeolite catalysts involves incorporation of a trivalent cation into a tetrahedral site of silica, with a proton generated for charge neutrality. Cations capable of this behavior on silica have a wide range of electronegativities, indicating that the generation of Bronsted acidity is not related to electronegativity. We suggest that Bronsted acid sites are associated with hydroxyl groups that bridge a supported metal cation and a Si^{4+} cation, and the acid strength can be related to the sum of the Pauling electrostatic bond strengths of the cations that are coordinated to this bridging hydroxyl group. We also are conducting isopropanol dehydration studies over our silica-supported oxide catalysts. It appears that catalysts with higher acid strengths are more active for this reaction, and that Bronsted acid sites may be more active than Lewis acid sites. We are conducting further kinetic studies and *in situ* infrared spectroscopy to document and explain these differences in catalytic properties.

Yale University
New Haven, Connecticut 06511

341. Studies in Carbon–Carbon Bond Activation/ Alkane Photoreactions with Mercury Vapor
R.H. Crabtree **$133,300**
Department of Chemistry **(16 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 showed that cyclopentanes can be dehydrogenated to cyclopentadienyl complexes by $[IrH_2(solv)_2L_2]$ cations. We have now shown that a similar reaction with *gem*-dimethylcyclopentane gives a dimethylcyclopentadiene complex. In addition we have found that 5,5-diethylcyclopentene gives 1,2- and 1,3-diethylcyclopentadienyl complexes by a route that involves alkyl migration from the ring to the metal and back. 3,3-dimethylcyclopentene gives a different type of reaction to give CH_4 and $(MeC_5H_4)IrHL_2^+$. The most interesting discovery is that mercury photosensitization can be made synthetically useful via a new apparatus that we have developed. An example of the sort of reaction we can bring about is: cyclohexane + methanol = cyclohexanemethanol + H_2.

342. Selectivity, Activity, and Metal–Support Interactions of Rhodium Bimetallic Catalysts

G.L. Haller **$92,000**
Department of Chemical Engineering

Metal–oxide and metal–metal interactions are being investigated using a combination of (1) physical characterization by x-ray absorption spectroscopies (EXAFS and XANES) and (2) chemical characterization by H_2 chemisorption, TPD, and catalytic reaction of varying structure sensitivity. EXAFS analysis of Rh/TiO_2 after high temperature reduction demonstrates direct Rh–Ti bonding, and XANES indicates a charge transfer from the reduced oxide to the metal. This charge transfer appears to have little effect of H_2 or CO chemisorption. Comparing rhodium to platinum on the same reducible support demonstrates that the platinum–oxide interaction occurs at a lower temperature and is stronger. Comparing rhodium on different supports (Rh/TiO_2 and Rh/V_2O_3) demonstrates that interaction with V_2O_3 is stronger than with TiO_2 and affects the kinetic parameters (e.g., activation energies) differently, which suggests there is an electronic consequence of the metal–oxide interaction.

343. The Role of d-Electrons in Chemisorption and Metal–Support Interactions Studied by Electron Spectroscopy

V.E. Henrich **$96,500**
Section of Applied Physics **(15 mo.)**

The nature of the interaction between small metal catalyst particles and transition-metal-oxide supports that occurs in strong metal–support interactions (SMSI) is being investigated by using model catalysts consisting of rhodium deposited onto single-crystal rutile TiO_2 supports in UHV. Surface-sensitive electron spectroscopies (UPS, XPS, Auger, EELS, and so forth) are used to study the electronic and geometric properties of the model catalysts and their chemisorption properties. Previous measurements showed that suboxide species migrate onto catalyst particles during high temperature reduction, blocking chemisorption sites. Recently we have shown conclusively that the presence of reduced titanium species (e.g., Ti^{3+} ions) on the surface of the support results in the transfer of electrons from the titanium ions to the rhodium particles, even in the absence of encapsulation. This charge transfer has been documented by several electron spectroscopic techniques, but ultraviolet photoemission observations of changes in Fermi level position provide the clearest evidence. This charge transfer, although significant for small metal particles, does not result in the changes in chemisorption properties that are associated with SMSI.

344. Energies of Organic Compounds

K.B. Wiberg **$97,000**
Department of Chemistry

This research project is designed to provide information on the energies and conformations of organic molecules via reaction calorimetry and theoretical calculations, and to use these data to improve empirical and semiempirical schemes (e.g., molecular mechanics) for estimating the properties of organic compounds. Heats of vaporization are being measured so that the thermochemical data may be corrected to the gas phase for proper comparison with the results of theoretical calculations. The data are also being used to explore steric effects and other structural effects on energies. Reactions being studied include the hydration of alkenes, the reduction of carbonyl compounds, and the hydrolysis of lactones and esters. Theoretical calculations are used to estimate the energies of interesting compounds, which have not as yet been prepared, and to study rotational barriers, nonbonded interactions, and other intramolecular interactions needed in molecular mechanics calculations.

Separations and Analysis

Aerospace Corporation
Los Angeles, California 90009

345. Isotopically Selective, Two-Step, Laser Photodissociation of Triatomic Molecules in Cryogenic Solutions

P.F. Zittel **$126,000**
Chemistry and Physics Laboratory

This research project is directed toward understanding photophysical, energy transfer, and chemical processes relevant to isotope separation by two-step laser photodissociation of small molecules. The two-step technique involves the excitation of molecules containing a chosen atomic isotope to an excited vibrational state by an infrared laser, followed by ultraviolet laser photodissociation, scavenging of the photofragments, and mass spectrometric analysis. Of particular interest are measurements of vibrationally state-specific photodissociation cross sections for different vibrational modes of a molecule. Initial room-temperature, gas-phase work has determined photodissociation cross sections for excited vibrational states of several small molecules and has led to separation of all stable isotopes of oxygen, carbon, and sulfur by two-step photodissociation of OCS. The two-step photodissociation method is now being extended to small molecules dissolved in cryogenic solvents where infrared absorption spectra and scavenging chemistry are qualitatively different from the gas phase. Larger isotope enrichment factors are sought as well as information about vibrational relaxation and chemical reactions in cryogenic liquids.

Auburn University
Auburn, Alabama 36849

346. Interfacial Chemistry in Solvent Extraction Systems
R.D. Neuman **$100,500**
Department of Chemical Engineering

Recent advances in spectroscopic techniques are being emphasized to yield novel information on the structure and dynamics of the macroscopic (liquid–liquid) interface and the microscopic (reversed micelles and microemulsion) interfaces that can exist in hydrometallurgical solvent extraction systems. Nuclear magnetic resonance, fluorescence, and photon correlation spectroscopic measurements have provided further support for earlier findings obtained from interfacial tension and mass transfer experiments that reversed micelles form in the system di(2-ethylhexyl)phosphoric acid (HDEHP)–n-hexane–$CaCl_2$ solution. These studies are being extended to include an organophosphonic acid (PC 88A), aromatic diluent (benzene), and different metal ions (Co^{2+}, Ni^{2+}, and Zn^{2+}) to determine whether reversed micellization is a general phenomenon occurring in solvent extraction systems that employ organophosphorus acids. The data obtained so far support this viewpoint. Preliminary drop-interface coalescence measurements have been performed, and an attempt is being made to correlate these results with various interfacial properties. The construction of a laser fluorescence apparatus for probing interfacial dynamics is nearing completion, and the laser heterodyne light scattering apparatus for measurements of interfacial viscoelastic properties is being optimized for high-resolution measurements.

Brigham Young University
Provo, Utah 84602

347. Novel Macrocyclic Carriers for Proton-Coupled Liquid Membrane Transport
J.D. Lamb **$77,140**
Department of Chemistry

We investigate macrocycle-mediated metal cation transport in hydrophobic liquid membrane systems of the bulk, emulsion, and supported types with the objective of separating cations. Research involves design, synthesis, and characterization of new, acidic macrocyclic carriers that permit the coupling of cation transport to the reverse flux of protons from an acidic receiving phase. Macrocycles of several basic designs are pursued, including pyridono-, triazolo-, phosphono-, and sulfonamide-based structures; the common feature is that the acidic group is part of the principal macrocyclic ring. Bulk membrane experiments have shown that several of these ligands have excellent flux and selectivity characteristics; these ligands are investigated further by pK_a and cation binding constant measurements. A second area of emphasis is the incorporation of macrocyclic carriers into liquid membranes supported on porous polymer films. We also investigate the effects of solvent and ligand partitioning between membrane and water phases, and the effect of specific ligand structural variations.

Brown University
Providence, Rhode Island 02912

348. Photochemical Generation of the Optoacoustic Effect
G.J. Diebold **$67,000**
Department of Chemistry

Experiments with the inverse optoacoustic effect have shown a nonlinear acoustic signal amplitude dependence on mole fraction of the absorbing gas. The most pronounced feature is a drop in signal amplitude with increasing mole fraction χ in the range from 0.1 to 1. Further experiments carried out with a CO_2 laser exciting sulfur hexafluoride showed even more dramatic effects. The most important feature of the response curve (near $\chi = 1$) has been explained with a thermal piston model, which shows the effect of thermal conduction to the windows of the spectrophone. Work is now in progress to explain the entire response curve from the region where the gas is optically thin ($\chi \ll 1$) to where it is optically thick ($\chi = 1$). The approach being investigated is solution of Sall's equation, which is equivalent to the coupled partial differential equations for temperature and pressure in the cell. An approximate solution is being investigated.

University of California
Los Angeles, California 90024

349. Multiheteromacrocycles That Complex Metal Ions
D.J. Cram **$125,000**
Department of Chemistry and Biochemistry

The general objectives of this research are to design, synthesize, and evaluate new types of cyclic and polycyclic organic ligand systems for their abilities to complex and lipophilize selectively guest metal ions. Correlations are sought between ligand structures and their binding free energies, their rates of complexation-decomplexation, and their solvation effects. Desired properties are high selectivity, rapid rates of complexation, and incorporation of detecting systems into the ligand. The principles of complementarity of host and guest and of host preorganization are being tested as guides in ligand design. Organized arrays of most of the functional groups of organic chemistry are being tested as ligating sites. Particular emphasis is placed on those systems that contain weakly basic nitrogen, sulfur in various oxidation states, and carbonyl groups of various types. Synthetic methods are being developed that lead to enforced preorganization of binding sites. Solvent effects on binding are being studied.

Columbia University
New York, New York 10027

350. Utilization of Magnetic Effects as a Means of Isotope Enrichment
N.J. Turro **$78,001**
Department of Chemistry

This research is aimed at developing novel methods for the separation of isotopes based on exploitation of differences in magnetic properties of isotopes. Emphasis has been placed on discovering reactions and conditions that allow the separation of isotopes that possess a finite magnetic moment from those that do not possess a magnetic moment. Successful systems have been designed for separation of ^{13}C (a magnetic isotope) from ^{12}C (a nonmagnetic isotope), and for the separation of ^{17}O (a magnetic isotope) from ^{16}O and ^{18}O (nonmagnetic isotopes). The restricted space provided by porous silica has proven to be an excellent environment for efficient separation of ^{13}C and ^{12}C based on the photolysis of dibenzyl ketone. The porous internal structure of zeolites is also an excellent environment for ^{13}C enrichment. The variation in zeolite structure offers a range of environments to serve for ^{13}C enrichment. A novel system, representing the most efficient yet discovered for ^{13}C enrichment, has been found for long-chain biradicals. In these cases the molecular chain serves as the analog of restricted space.

University of Delaware
Newark, Delaware 19716

351. Studies of the Analyte–Carrier Interface in Multicomponent Flow Injection Analysis
S.D. Brown **$80,000**
Department of Chemistry

The use of flowing streams to transport injected analytes has received considerable attention lately. Situations where the injected analyte reacts with reagents present in the carrier stream have received almost no study. This project involves the study of product distributions with an injected bolus. Initial studies have focused on the characterization of the flow reactor and on the development of software for the analysis of mixtures and for the study of reaction kinetics. These studies will be useful in analyses of the distribution of reaction products across the interface of the injected bolus and the carrier stream in flow injection analyses.

George Washington University
Washington, District of Columbia 20052

352. New High-Temperature Plasmas and Sample Introduction Systems for Analytical Atomic Emission Spectrometry
A. Montaser **$65,000**
Department of Chemistry

New high-temperature plasmas and new sample introduction systems are developed for rapid elemental analysis of solutions and solids using atomic emission spectrometry. These devices offer promise of solving singularly difficult analytical problems that exist now or are likely to arise in the future in the various fields of energy generation, environmental pollution, biomedicine, and nutrition. Emphasis is placed on: (1) generation and fundamental investigation of annular helium inductively coupled plasmas suitable for the excitation of high-energy spectral lines, to enhance the detecting powers for a number of elements; (2) generation of plasmas that require low gas flows and low input power, to decrease the cost of analytical determination; and (3) development and characterization of new sample introduction systems that consume microliter or microgram quantities of samples. Investigations include fundamental principles behind the measurements, evaluation of the analytical potentials of the devices developed, and demonstration of the analytical methods in representative samples.

Georgetown University
Washington, District of Columbia 20057

353. Study of the Performance of a New Detector Class for Liquid Chromatography
G. Guiochon **$57,290**
Department of Chemistry

We will study a new class of detectors for liquid chromatography. The general principle of these detectors uses nebulization of the column effluent in a stream of tepid gas where the solvent is vaporized. The nonvolatile solutes form small particles that are carried by the gas stream across an intense light beam. Light scattered by the particles is a function of their size (i.e., of the concentration of nonvolatile solutes in the column effluent). The research involves studies on the nebulization of the column effluent (comparison among results obtained with a concentric nebulizer, an ultrasonic nozzle, and a pierced diaphragm), on the light scattering (influence of the light beam energy and wavelength), and on the acquisition mode of the signal (continuous beam versus pulsed beam with a box-car amplifier). We will also investigate alternative methods to detect the solutes by separating particles of nonvolatile material from the stream of gas and vapor.

Georgia Institute of Technology
Atlanta, Georgia 30332

354. Fundamental Studies with a Monodisperse Aerosol-Based Liquid Chromatography/Mass Spectrometry Interface (MAGIC-LC/MS)
R.F. Browner **$132,000**
Department of Chemistry **(24 mo.)**

An aerosol-based liquid chromatography/mass spectroscopy interface (MAGIC-LC/MS) has been constructed. This device uses monodisperse aerosol generation, atmospheric pressure desolvation, and aerosol beam separation of solute particles and solvent vapor. The interface may be operated with equal ease on magnetic sector or quadrupole instruments. The device is very simple to operate, and has minimal adjustments for setup. The interface may be connected to the mass spectrometer without modification to the instrument, and allows a complete choice of electron impact or chemical ionization modes. The interface has perfomed well with microbore chromatography, and can be operated with all commonly used normal and reversed phase solvents. Tests with a number of environmentally important compounds, such as carbamate and triazine pesticides and polynuclear aromatic compounds, have given detection limits of approximately 100 pg with single ion monitoring, with 1 to 10 ng for full EI scans.

Hampton University
Hampton, Virginia 23668

355. Use of Ion Chromatography–D.C. Plasma Atomic Emission Spectroscopy for the Speciation of Trace Metals
I.T. Urasa **$70,000**
Department of Chemistry **(18 mo.)**

The project objectives are (1) to study the factors that influence the use of d.c. plasma atomic emission spectrometry (DCPAES) as an element-specific detection method (ESD) for ion chromatography (IC); and (2) to tailor the combined analytical system to speciation of trace elements. The use of ESD has the following advantages: (1) response of the detector to a specific element can lead to an improved chromatographic analysis especially when only partial separation of the mixture components is achieved; (2) measurement sensitivity can be improved; and (3) interference and matrix effects can be eliminated. The potential of DCPAES as a chromatographic detector has not been fully developed and exploited. This detection approach has an added advantage in multielement measurement capability suitable for determining metals and nonmetals. In this research the system will be evaluated as a detector for IC effluents consisting of selected species of arsenic, chromium, iron, manganese, nickel, and vanadium. The fundamental hypothesis is that DCPAES can serve as a sensitive ESD for IC allowing the separation and detection of a variety of species of elements (metals and nonmetals) at a wide range of chromatographic conditions. Work will focus on the study and development of chromatographic conditions and IC-DCPAES coupling mechanisms that allow maximum detection capability.

University of Houston
Houston, Texas 77004

356. *Mechanisms of Thickening, Cake Filtration, Centrifugation, and Expression*

F.M. Tiller **$140,000**
Department of Chemical Engineering **(17 mo.)**

The theory of particulate separation involving compressible, porous beds or sediments as found in sedimentation, filtration, centrifugation, and expression is studied. The Darcy equation in spatial or material coordinate form must be combined with a differential momentum balance to produce simultaneous equations involving the liquid pressure and the compressive effective pressure. Solution of these equations requires constitutive relations involving permeability, specific flow resistance, and porosity. Different boundary conditions, the presence of gravitational or centrifugal forces, and solid movement in sedimentation lead to different forms of the basic equation. This project aims to unify the theory underlying the different types of solid–liquid separation and to develop techniques for determining empirical parameters involved in the constitutive equation. The structures of beds of dispersed and aggregated uniform, micron-sized particles are related to compressibility. Based on particle size, shape, and degree of aggregation, a rough predictive method for calculating parameters in functions relating porosity and permeability to effective pressure has been developed. CAT scans are being used to study transient sedimentation and cake uniformity. A new approach to the theory of continuous thickening has been developed. Pressure distributions are used to study flow mechanisms and fine particle migration.

University of Idaho
Moscow, Idaho 83843

357. *The Effect of Electric Fields on Liquid Extraction*

T.E. Carleson **$25,000**
Department of Chemical Engineering

The objectives of this research are the determination of a theoretical model and the experimental verification of the model of the effect of electric fields on a small-scale liquid extraction column. Various studies with single conducting drops in an insulating medium indicate that an applied electric field can significantly change the drop size and terminal velocity. For an electric field oriented in the direction of gravity and charged drops with a density higher than the continuous phase, the drop size is reduced and velocity increased with an increase in field strength. Incorporation of the electric field force into a force balance on the forming and falling drop results in a fairly good model for prediction of the effect of the electric field on the drop size and velocity. Incorporation of these parameters into a standard mass transfer model of the drop extraction process also appears to allow prediction of the extraction for single drops. A multistage sieve tray extraction column has been used to determine the effect of an electric field on a drop population and extraction.

University of Illinois
Urbana, Illinois 61801

358. *Theta Pinch Discharges for Solids Vaporization and Elemental Chemical Analysis*

A. Scheeline **$85,000**
School of Chemical Sciences

A pulsed, magnetically constricted plasma (theta pinch) is being used for elemental chemical analysis. The pinch is used to heat and compress a plasma, generally of argon. With correct sample placement, the plasma vaporizes a few micrograms of the sample with each pinch. Recently, useful emission has been observed not only from conductive solids (aluminum, stainless steel) and powders (tungsten), but also from bulk insulators (boron nitride and alumina). The sampling of these refractory materials is an indication that the goals of this research are being achieved. The only other analytical method that can sample bulk insulators without premixing with a conductive powder is laser ablation. Because the sampling is over a larger area with the theta pinch than with laser ablation, reduced sensitivity to problems caused by sample heterogeneity is anticipated. Time gating allows observation of emission by neutral atoms for hundreds of microseconds after ionic emission and continuum emission have disappeared, making low limits of detection likely. Immediate plans are to extend past qualitative successes to quantitative results.

Kansas State University
Manhattan, Kansas 66506

359. Development of a New Novel Hadamard Transform Infrared Spectrometer for Analytical Chemistry

W.G. Fateley **$60,000**
Department of Chemistry

We are developing a special Hadamard infrared spectrometer to investigate the heterogeneous nature of substances such as coal samples. A newly designed Hadamard mask is used. A two-dimensional infrared study will investigate the distribution of impurities, structural differences, material properties, and concentration variations in coal and other heterogeneous materials. In this study we use a two-dimensional Hadamard fore mask accessory to the HTS spectrometer. The coals serve as the source in an emission experiment and are placed between the focusing optics and the two-dimensional Hadamard fore mask in a transmission experiment. The chemical variations with depth will be investigated in different coal samples. Using the photoacoustic detector and a Czerny-Turner monochromator equipped with an exit Hadamard mask allows depth-profiling of these coal samples. Using subtraction techniques developed in Fourier transform spectroscopy, we will examine the spectra of different depths and the chemical differences between the surface and the bulk of these coal samples. These investigations may be classified as two-dimensional depth spectroscopy. Additional studies involving the development of a Fourier transform spectrometer and a Hadamard transform spectroscope for Raman studies are in progress. A Nd:YAG laser is the exciting source. The studies yield important structural information.

Kent State University
Kent, Ohio 44242

360. Adsorption and Desorption of Hydrocarbons at Low Concentrations

R. Madey **$90,000**
Department of Physics

The aim of this research is to study the adsorption and diffusion of gases through porous media adsorber beds. The approach involves calculations based on a mass-balance equation of the quantity of adsorbate adsorbed on an adsorbent, measurements of adsorption isotherms of hydrocarbons on activated carbon and polystyrene beads at selected temperatures, and studies of the dynamics of breakthrough curves with both a step-function and a pulse change of the input concentration. The breakthrough curves of binary mixtures exhibit interference phenomena where the output concentration of the weakly adsorbed component increases above the input concentration until the other component elutes. The project objectives include (1) providing an explanation of interference phenomena and (2) studying adsorption with a first-order irreversible chemical reaction. Since the decay of a radioactive isotope is a first-order reaction, measurements of the transmission of radioactive ^{41}Ar and stable ^{40}Ar will permit a study of the effect of dynamic parameters on the steady-state transmission and on the moment of the transmission curve. Transmission is the ratio of the concentration of an adsorbate at the bed outlet to that at the inlet.

Lehigh University
Bethlehem, Pennsylvania 18015

361. Polymer-Based Catalysts

S.L. Regen **$63,000**
Department of Chemistry

This research is aimed at developing new and improved polymer-based catalysts and selective chemical transformations. Specific chemical objectives include: (1) the entrapment of metal colloids within porous and nonporous polymerized vesicles and an examination of their resulting activity, stability, and size-selectivity toward alkene hydrogenation; (2) the incorporation of soluble transition metal complexes within polymerized vesicle membranes and the measurement of their ability to promote regio- and size-selective catalytic hydrogenation; (3) the construction of receptor sites within polymerized vesicle membranes; and (4) the extension of the "vacillating-reaction" principle to catalytic systems.

University of Maryland
College Park, Maryland 20742

362. Study of Highly Selective Sorptive Effects with Applications to Paraffins and Petroporphyrin Separations

D.H. Freeman **$60,600**
Department of Chemistry

Organic biomarkers are of interest in areas that create a challenge to modern separation science. New sorptive materials and new uses of methodological principles are being studied to assist the isolation of biomarkers that are geochemically interesting. These efforts are focused on two goals. The chemical selectivity of silicalite, a zeolitic form of silica, is highly sorptive for the n-alkanes and their monomethylalkane isomers. Molecules of slightly larger cross-sectional diameter are selectively excluded. Diffusion studies are aimed at thermal and solvent effects on the processes of adsorption and desorption. The second major goal is the isolation of geoporphyrins. Selectivity multiplying sequences of short HPLC columns (1 to 10 cm length, 50 to 500 plates) are being studied. Different metalloporphyrin groups are isolated. Their tetrapyrrole ring structures are identified by spectrophotometry. Group subclassification is based on interactions with a series of sorbents being screened for that purpose. Automated procedures are being developed where possible. A suite of characterized petroleum and shale oil samples are being examined. The basis for isolating pure metalloporphyrins from the New Albany shale is being developed.

University of Minnesota
Minneapolis, Minnesota 55455

363. Continuous Reaction Chromatography

R. Aris, R.W. Carr **$70,000**
Department of Chemical Engineering and Materials Science

Continuous reaction chromatography is a method for carrying out chemical reaction with simultaneous chromatography of reactants and products in a single continuous flow reactor, by providing a relative motion between the chromatographic packed bed and the feedstream. We have completed (1) investigations of the rotating cylindrical annulus for liquid-phase reaction with a solid adsorbent and gas–solid catalytic reactions and (2) a detailed modeling study of the behavior of a countercurrent moving-bed chromatographic reactor. Experimental tests of laboratory-scale countercurrent moving-bed reactors are being conducted and some results have been reported. 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 also being investigated both theoretically and experimentally. It has been shown that the switched bed gives a better performance than the fixed bed and can emulate the continuous countercurrent moving bed. A small switched column has been built and is currently being tested as an adsorber before being run as a reactor.

National Bureau of Standards
Gaithersburg, Maryland 20899

364. Competitive Ion Kinetics in Direct Mass Spectrometric Organic Speciation

L.W. Sieck **$135,000**
Center for Chemical Physics

This research project involves the measurement of fundamental properties of gas-phase ions, including fragmentation and reaction mechanisms and rates, structures, and the thermochemistry associated with ionization, protonation, deprotonation, and reaction. When appropriate, this information is used to suggest chemical ionization techniques that incorporate competitive ion kinetics and permit identification and/or assay of specific compounds or classes of compounds occurring in complex organic mixtures, with emphasis on the interpretation of Thermospray spectra. The experimental project uses the National Bureau of Standards pulsed high-pressure mass spectrometer system as the prime facility; a triple MS instrument is also available. Work in progress includes determinations of enthalpies of hydration and solvation of complex anions, systematic studies of the unimolecular kinetics associated with ion pyrolysis, and measurements of the temperature dependence of reaction rates. Ion–molecule reactions pertinent to the plasma etching of semiconductor materials are also under investigation, with emphasis on the role of impurities.

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

365. Stable Isotope Studies

T. Ishida **$88,000**
Department of Chemistry

This project is concerned with fundamental studies of isotope effects and their applications to problems of stable isotope fractionation. The following studies have recently been completed: (1) cell-model analyses of vapor pressure isotope effects in liquid and solid ammonia and in liquid methylene difluoride, and (2) development of a self-contained chemical recycle system for use in the ^{15}N fractionation processes, eliminating the need for external chemical feeds and chemical waste disposal. Current areas of investigation are: (1) basic and developmental studies of heterogeneous catalyses for the hydrogen isotope exchange reaction between water and hydrogen with *in situ* controllable hydrophobicity and *in situ* catalytic activity regeneration; (2) molecular dynamics (MD) simulations of physical spectroscopic properties of liquid and solid ammonia (as a basis for further MD studies of solutions in liquid ammonia) and of catalytic properties of the platinum surfaces for hydrogen isotope exchange reactions; and (3) continued development of zero-point energy additivity tables for organic molecules.

University of North Carolina
Chapel Hill, North Carolina 27514

366. Solid-State Voltammetry and Sensors in Bases and Other Non-Ionic Media

R.W. Murray **$84,000**
Department of Chemistry

We will employ solid-state polymeric materials as the charge-transporting media between closely spaced (micron and submicron) electrodes, with the electrodes and polymer in contact with a bathing gas or vapor, or a non-ionic fluid. Focus is on the properties of electrochemical and electrocatalytic reactions that are customarily studied in contact with liquid–electrolyte solutions when these reactions are deprived of liquids and external electrolytes. We also plan to develop the experimental means to conduct liquidless electrochemical experiments (which we call solid-state voltammetry) that can take advantage of the diagnostic quantitative relations (transport, thermodynamic, electrode kinetic) that have been developed to understand electrochemical reactions occurring in liquid–electrolyte solutions.

University of Oklahoma
Norman, Oklahoma 73019

367. A Study of Micellar-Enhanced Ultrafiltration

J.F. Scamehorn, **$70,000**
S.D. Christian
School of Chemical Engineering and Materials Science

In micellar-enhanced ultrafiltration (MEUF), surfactant is added to an aqueous stream. The surfactant forms aggregates called micelles containing approximately 100 molecules. Organic solutes dissolved in the water tend to solubilize or dissolve in the core of the micelles, while multivalent cationic metals tend to adsorb on the micelle surface if the surfactant is anionic. The solution is then treated by an ultrafiltration device with membrane pore sizes small enough to block the micelles with the associated organic compound or metal ion. The ability to individually or simultaneously remove both organics and metal components is a major advantage of MEUF. MEUF has been shown to result in high rejections and high relative flux rates in removal of phenolics and divalent heavy metals. A very pure permeate stream and a concentrated retentate stream result from this process. For example, in the removal of *tert*-butyl phenol or copper(II) from solution, the resulting permeate can obtain concentrations of the two pollutants, which are two orders of magnitude less than in the feed. The permeate/feed ratio can be 90%. Traditional concentration polarization behavior is observed under reasonable conditions for MEUF.

Oklahoma State University
Stillwater, Oklahoma 74078-0447

368. Unsegmented Continuous Flow Sample Processing and Electrochemical Detection and Determination of Gaseous Species

H.A. Mottola **$68,000**
Department of Chemistry

This work involves a novel approach to sample processing in determining gaseous pollutants of oxidizing and reducing nature. A continuous-flow unsegmented all-gas carrier system and a segmented liquid–gas interface system will be constructed for sample introduction and transport to the detection/determination port. A regenerable electrode probe based on the redox characteristics of the iron(II) and iron(III) complexes with 1,10-phenanthroline and related ligands will be implemented as the detection device. Several electrodes of the chemically modified type will be constructed and tested. Amperometric and coulometric current measurements will be evaluated for acquisition of the analyte signal for quantitative purposes. Voltammetric studies will provide evaluation of the electrode surfaces generated as part of the work.

Purdue University
West Lafayette, Indiana 47907

369. Reactions of Gaseous Metal Ions/Their Clusters in the Gas Phase Using Laser Ionization: Ion Cyclotron Resonance Spectroscopy

B.S. Freiser **$160,000**
Department of Chemistry **(18 mo.)**

Our recent developments (involving both software and hardware modifications of the Nicolet FTMS-1000 Fourier transform mass spectrometer) now enable us to conduct research in what can be properly termed a complete gas-phase chemical laboratory. Selected ions of interest can be mixed with various reagents and their detailed chemistries monitored through a series of as many as eight reaction sequences. At any point in these sequences, ion structures can be elucidated and fundamental kinetic and thermodynamic parameters of the reactions can be determined. We are currently examining the gas-phase chemistry and photochemistry of metal ions, metal ion clusters, and metal ion complexes, all of which have a bearing on the fundamentals of catalysis.

Rensselaer Polytechnic Institute
Troy, New York 12180

370. Macrocyclic Ligands for Uranium Complexation

K.T. Potts **$92,000**
Department of Chemistry

A computer-aided design (CAD) approach has been used in the design of a series of macrocyclic ligands whose cavity diameters were optimized for the complexation of the uranyl (UO_2^{2+}) ion from solutions. These macrocycles, assisted by the "macrocyclic effects" and incorporating oxygen or sulfur as the ligating atoms, should show selectivity for the uranyl ion and give complexes with favorable stability constants. Focus is on three principle types of macrocycles: cycloaliphatic-type systems containing one biureido function and two acyl urea functions; cycloaliphatic-type systems containing three biureido functions; and systems of the above type containing both aromatic and heterocyclic subunits. We have developed synthetic sequences leading to macrocyclic precursors, using novel applications of acyl isocyanate chemistry. Reactions are characterized by economy in operation and by the high yields obtained. Our target macrocycles will be studied for their selectivity in absorbing the uranyl ion from both homogeneous and heterogeneous systems. The structures of these uranyl complexes, together with their stability constants, will be determined. These macrocycles will all have important potential applications in two main areas of uranium technology: the removal of uranium from waste streams and the development of alternate sources of uranium by extraction from natural waters such as seawater and river systems rich in dissolved uranium.

San Diego State University
San Diego, California 92182

371. Development and Optimization of Methodologies for Analysis of Complex Hydrocarbon Mixtures

R.J. Laub **$83,000**
Department of Chemistry

In this project, the analytical and physicochemical properties of nonelectrolyte solutions are determined and interpreted in terms of solute liquid–gas (GC) and liquid–liquid (LC) activity and partition coefficients as well as gas-phase virial effects. Regressions of the former against the composition of multicomponent solvents are examined from the standpoints of solvent–additive interaction, solvent–solvent self-association, and, in each case, weak-to-strong solute–solvent complexation. Also of very considerable interest are newly synthesized polymeric side-chain liquid–crystalline (MEPSIL) systems. Those fabricated thus far include several that are nematic over a temperature span in excess of 200°. Others are chiral; while still others appear, simultaneously, to exhibit properties of both types of mesomorphs. The MEPSIL materials also yield unprecedented analytical separations when employed as GC or LC stationary phases.

Syracuse University
Syracuse, New York 13244

372. Mechanisms of Gas Permeation Through Polymer Membranes

S.A. Stern **$84,000**
Department of Chemical Engineering and Materials Science

The project objective is to investigate the significant changes that commonly occur in the solution and transport behavior of gases in polymer membranes at their glass-transition temperature (T_g). To explore the character of these changes, permeability, diffusion, and solubility coefficients for CH_4, C_2H_6, η-C_4H_{10}, and CO_2 in poly(butyl methacrylate), (PηBMA, T_g = 27 to 35°C), have been determined at temperatures from -25 to 50°C and at pressures up to 25 atm. Contrary to expectations, the permeability, diffusion, and solubility coefficients for CH_4, C_2H_6, and η-C_4H_{10} did not exhibit the transition to "dual-mode sorption" behavior below T_g reported for simple gases in many glassy polymers. Only in the case of CH_4 was such incipient behavior observed at -25°C. The absence of dual-mode sorption effects is attributed to the fact that the metastable "excess" free volume in glassy PηBMA required for such effects is very small, as indicated by the small difference in the coefficients of thermal expansion of "rubbery" and glassy PηBMA. Because the excess free volume in the polymer increases as the temperature is lowered, dual-mode sorption of CH_4, C_2H_6, and η-C_4H_{10} should manifest itself at lower temperatures, as was observed with CH_4 at -25°C, unless the polymer is strongly plasticized by the penetrant gases.

373. *Particle Deposition in Granular Media*

C. Tien **$182,500**
Department of Chemical Engineering and Materials Science **(24 mo.)**

The principal objective of this study is to elucidate the various phenomena arising from the flow of aerosol suspensions through and the deposition of aerosols in granular media. The project focuses on (1) experimental investigation of the transient behavior of aerosol filtration in granular filters, (2) development of algorithms for predicting aerosol filtration in fluidized beds, (3) aerosol collection in magnetically stabilized fluidized filters, (4) *in situ* observation of aerosol deposition in two-dimensional model filters, and (5) experimental study of cross-flow moving-bed granular filtration.

University of Tennessee
Knoxville, Tennessee 37996-1600

374. *Dual Mechanism Bifunctional Polymers: Design, Synthesis, and Application of a New Category of Metal Ion Complexing Agents*

S.D. Alexandratos **$75,000**
Department of Chemistry

A new category of resins, dual-mechanism bifunctional polymers, has been synthesized. The primary application for these resins is recovery of metal ions from aqueous streams using solid–liquid extraction schemes. They can be effectively used in hydrometallurgical processes and are especially important for strategic metal recovery. These resins consist of a polystyrene support network on which are bonded two different functional groups. Bifunctionality is utilized to endow the polymer with selectivity towards one or a few metal ions. Three classes of resins within this new category are being developed. The first class consists of the ion-exchange/redox resins, which allow for the recovery of pure metal from a solution of its ions when the ion has a reduction potential greater than +0.3 V. The second class of resins incorporates specific coordinating ligands to yield the ion-exchange coordination resins. Such ligands include amines, esters, and polyethylene glycols. The third class of resins are the ion-exchange/precipitation-resins, which incorporate anions in proximity to the cation exchange sites, thus allowing for the precipitation of cations such as cadmium and nickel. Metal-ion selectivity series have been established for the different resins, as has their superiority over the sulfonic acid resins. For example, the phosphinic acid resin shows log D values for iron, mercury, silver, and manganese of 3.5, 2.5, 1.3, and 0.7 under conditions (1N HNO_3/3N $NaNO_3$) where the sulfonic resin shows values of 0.9, 0.5, 1.0, and 0.5, respectively.

375. *Capillary Liquid Chromatography Using Laser-Based and Mass Spectrometric Detection*

M.J. Sepaniak **$64,000**
Department of Chemistry

The focus of this research is the development of capillary liquid chromatography (LC) as a practical separation technique for the analyses of volume-limited complex samples and for difficult to resolve compounds. Although moderately efficient slurry-packed fused silica capillary columns and true open capillary columns have been prepared, the emphasis of our capillary LC work has been on the development and characterization of micellar electrokinetic capillary chromatography (MECC). With this technique, solutes are separated based upon their differential distribution between an electro-osmotically pumped mobil phase and an electrophoretically retarded micellar phase. We have routinely achieved efficiencies of greater than 100,000 plates/meter for rapid separations. Factors that influence column efficiency have been extensively studied. In this regard, the MECC technique exhibits characteristics that are common to both packed and true open capillary LC. Factors that affect column selectivity (e.g., micelle type) have also been studied. Elution range with the technique has been extended through silanation of the column surface. This should facilitate the separation of complex samples. Because eluted solute bands have very small volumes (typically 50 to 300 nL), detection in MECC is complicated. Whenever possible, laser-based fluorescence detection has been employed. However, efforts are in progress to develop a fiber-optic-based, evanescently coupled absorbance detector for the technique. We have also begun to explore the interfacing of the technique to mass spectrometry.

University of Texas
Austin, Texas 78712

376. *Synthesis and Analysis of Novel Polymers with Potential for Providing Both High Permselectivity and Permeability in Gas Separation Applications*

W. Koros, D. Paul **$75,000**
Department of Chemical Engineering

This project involves a concerted experimental program to develop advanced polymeric membranes for gas separation applications. Focus is on the interpretation of high-pressure pure and multicomponent gas sorption and transport data to be collected for a series of novel polymers to be synthesized as part of the project. The research builds on earlier work showing remarkably high permeabilities and selectivities for important gas pairs using rigid, high glass transition polymers that contain bulky groups and other features to prevent tight segmental packing. The study includes the pressure regime in which serious plasticization (softening) is anticipated, and mixed gas permeability measurements will track the loss in selectivity as the various polymers become plasticized. Existing theories and types of correlations for the fundamental sorption and diffusion coefficients of the various penetrants will be tested for these novel rigid molecularly open materials. Such tests will indicate the suitability of these theories and correlations to guide material selection and design of advanced gas separation modules. The project also includes research to identify suitable solution formulations for casting asymmetric membranes from attractive candidate materials discovered in the preliminary phase of the work.

Texas A and M University
College Station, Texas 77843-3255

377. Laser-Ion Beam Photodissociation Techniques

D.H. Russell **$98,900**
Department of Chemistry

This project emphasizes laser-ion beam photodissociation methods for probing the dynamics of dissociation reactions of highly activated ionic systems. The experimental hardware and methods are being developed by using model chemical systems such as $C_6H_6^+$ and $C_4H_4^+$, which are relatively well characterized, and new systems such as $Fe_x(CO)_y^+$ and similar ionic cluster fragments. In addition, the potential analytical utility of laser-ion beam photodissociation for the structural characterization of large biomolecules is being evaluated. These latter studies are being performed on ions formed by fast-atom bombardment (FAB) ionization and include molecules such as chlorophyll a, vitamin B_{12}, small peptides, and glycopeptides (1,500 to 4,000). These studies are performed on modified analytical instruments (e.g., Kratos MS-50TA and MS-902) as well as a Fourier transform mass spectrometer (Nicolet FTMS-1000).

University of Texas at El Paso
El Paso, Texas 79968-0513

378. Macrocyclic Lanthanide Ion Selective Reagents

C.A. Chang **$51,950**
Department of Chemistry

A systematic study of the thermodynamic and kinetic stabilities of lanthanide complexes of two groups of ionizable macrocyclic ligands is now under way. One group includes ligands that are all derivatives of diaza-15-crown-5 and diaza-18-crown-6 with varying number and type of ionizable functional groups. The other group includes ligands that are all cyclic diester derivatives of EDTA with different cavity sizes. Effects of the number and length of ionizable functional groups, stereochemical constraint, and cavity size will be examined. A primary goal is to construct a relationship between the thermodynamic stability and the kinetic stability. Several postulates regarding the mechanisms of complex formation and dissociation have been proposed, and may have predicting power if validated.

Texas Tech University
Lubbock, Texas 79409

379. Use of Functionalized Surfactants and Cyclodextrins in Chemical Analysis

D.W. Armstrong **$73,000**
Department of Chemistry and Biochemistry

A new technique of micelle-mediated resonance Raman spectroscopy (MMRRS) has been developed in our laboratory. Ordinary Raman scattering spectrometry produces vibrational spectra that provide abundant information on the structure of molecules. The major shortcoming of this potentially powerful technique is the inherent weakness of the Raman signal. Laser excitation on an electronic absorption band can enhance the weak Raman signal (i.e., a resonance effect). Unfortunately, this frequently produces highly fluorescent backgrounds that negate the resonance Raman signal. Using specially functionalized micelles we have made resonance Raman spectroscopy into a sensitive and generally applicable technique in which an analyte's luminescence properties are no longer of major concern. There are five modes of micellar action, all of which can produce beneficial effects. There is frequently a synergistic effect when two or more modes of action occur at one time. We are currently evaluating the mechanistic aspects of this work and developing several practical applications. Field Flow Fractionation (FFF) was introdued by Giddings in 1966. The overall range of FFF is about 12 orders of magnitude, from about 10^4 to 10^{16} molecular weight. Small-to-moderate molecular-weight solutes are difficult or impossible to separate by FFF. We can extend the range and selectivity of FFF by using secondary chemical equilibrium. The theory has been elucidated and experimental verification is in progress.

380. Metal Ion Complexation by Ionizable Crown Ethers

R.A. Bartsch **$100,500**
Department of Chemistry and Biochemistry

The goals of this research are the synthesis of lipophilic crown ethers with pendant ionizable groups and the application of these compounds for selective metal ion complexation. A variety of lipophilic ionizable crown ethers are being prepared in which the following structural features are systematically varied: (1) the size of the polyether cavity; (2) the number and types of ethereal oxygens in the crown ether ring; (3) the attachment site(s) for lipophilic groups; (4) the presence or absence of aromatic groups as polyether ring substituents; (5) the type of ionizable group; and (6) the number of ionizable groups. The ionizable functions include carboxylic, phosphonic, and sulfonic acid groups. The efficiencies and selectivities of these lipophilic ionizable crown ethers in competitive solvent extraction, in liquid surfactant (emulsion) extraction, and in bulk liquid membrane and polymer-supported liquid membrane transport of alkali metal, alkaline earth, and transition metal cations are being assessed.

381. Novel Approaches to Ionic Chromatography

P.K. Dasgupta **$80,500**
Department of Chemistry and Biochemistry **(13 mo.)**

The project objective is to discover analytical techniques for high-resolution, high-sensitivity chromatographic analysis of ions. For chromatographic detection of heavy metals, an extensive study of fluorogenic ligands has been made. Particularly promising were sulfoxine, lumogallion, and morin. The fluorescence properties of the reaction products of 78 metal species (including oxidation state variations) with sulfoxine (8-hydroxyquinoline-5-sulfonic acid) were investigated; 42 of these fluoresce, many intensely. Using the ligand in-eluent of postcolumn, subpicomole detection of several metals has been demonstrated. Extensive studies have been made of micellar and organic solvent enhancement of metal–sulfoxine fluorescence and the effect of quenching ions on the same. The study of ligands that form intensely colored complexes continues, with special attention on those that are particularly amenable to detection at wavelengths emitted by solid-state electroluminescent emitters. Theoretical and experimental advances have been made for absorbance amplification at low absorbance levels using etalon-based cells. Fundamental studies have been made on mixing noise induced by various postcolumn reactor designs. In the area of anion chromatography, studies of membrane suppressors and postsuppressors have continued. Hydroxide eluent gradient anion chromatography has been shown to be particularly attractive; pH detection is viable and sufficiently sensitive in many cases. Present research involves exchanging the sample analyte for a more easily detectable ion via a postsuppressor membrane-based ion exchanger.

University of Utah
Salt Lake City, Utah 84112-1183

382. Pulsed Laser Photothermal Spectroscopy of Liquids and Solids
E.M. Eyring **$78,000**
Department of Chemistry

Pulsed laser photothermal spectroscopies have developed less rapidly than microphonic photoacoustic spectroscopy (PAS). However, the pulsed photothermal methods have several intrinsic advantages over microphonic PAS, such as the capacity for time resolving faster chemical events and easier avoidance of background noise in the desired photothermal signals. A careful comparison is being made of existing theory with experiment in pulse laser photothermal spectroscopy of liquids. The dependence of the PA pressure on thermal and elastic properties of the liquid, on laser-beam-transducer geometry, on the speed of sound, and on temperature is being determined experimentally. Both optical detection and a fast, polymeric foil, piezoelectric detector are being used in conjunction with a Nd:YAG pumped, wavelength tunable, pulsed dye laser to excite the sample. Further understanding of this technique will facilitate the determination of deexcitation pathways and their quantum yields in liquids and transparent solids. In a parallel study the same pulsed laser system will be used to explore the potential of pulsed photothermal radiometry (PPTR) for time resolving relaxation processes in solids. Pure powdered dyes and the same dyes diluted with KBr will be compacted into sample pellets to determine the dependence of the PPTR signal on absorption of the laser light pulse by the dye. A better understanding of PPTR signals in simple solids should have future application in the study of technologically important solids, such as the thermochromic polydiacetylenes.

383. Hydrophobic Character of Nonsulfide Mineral Surfaces as Influenced by Double Bond Reactions of Adsorbed Unsaturated Collector Species
J.D. Miller **$70,000**
Department of Metallurgy and Metallurgical Engineering

The separation of nonsulfide minerals from ore is frequently accomplished by froth flotation using unsaturated fatty acids as collector. Variables such as temperature, oxygen partial pressure, and solution chemistry may have a significant effect on flotation rate and the hydrophobic character of certain nonsulfide minerals. Bubble attachment measurements at a fluorite (CaF_2) surface have shown that attachment times decrease by an order of magnitude at higher temperature and higher oxygen partial pressure when compared to ambient conditions. Adsorption density measurements indicate that chemisorption reactions occur between oleate and the fluorite surface. At higher temperature and oxygen potential the adsorption density increases slightly. More important, however, is the finding from infrared spectroscopy that the carbon–carbon double bond is reduced in intensity under these conditions, indicating a specific interaction of the adsorbed unsaturated collector species. It has been established that the oleate interaction at the fluorite surface consumes oxygen, and the heat of the reaction has also been measured by a microcalorimetic technique. Study of the nature of this interaction by *in situ* FTIR is in progress. It is thought that the interaction may involve surface polymerization; if such a reaction is operative, the implications are far reaching. Catalysts or new collectors can be developed to improve the performance, selectivity, and energy economy in nonsulfide mineral flotation systems. Some recent results suggest that such reactions can be catalyzed at the surface of collophanite.

University of Virginia
Charlottesville, Virginia 22901

384. Glow Discharge as an Atomization and Ionization Source
W.W. Harrison **$157,200**
Department of Chemistry **(24 mo.)**

The glow discharge is used in our laboratory as an atom reservoir for excitation and ionization processes in analytical spectroscopy. We are primarily developing glow discharge mass spectrometry (GDMS) as a trace elemental analysis method in solid samples. Focus is on new types of ion source designs, optimization of plasma sampling, and the elucidation of interferences arising from the polyatomic combinations in the glow discharge. We are examining relative sensitivity factors in metal and alloy samples, and attempting to determine the factors most responsible for certain sensitivity variations from sample to sample. Geological materials are also of interest due to the specialized sample-handling requirements and the potential opportunities for study of matrix host materials and their interactions with plasma constituents. We are using powdered graphite, silver, and aluminum in varying proportions to examine model compounds, notably mixed metal oxides representing simulated geological samples. Real geological materials such as soils, ores, and minerals are studied for sensitivity and precision. Resonance ionization studies involving an excimer laser and dye laser are continuing to probe the atomic populations produced by the glow discharge. Special emphasis is on the study of metastable argon states and their role in ionization of sputtered sample atoms. We also use the laser to ablate sample atoms into a glow discharge for subsequent ionization. An overall goal of our work is a more comprehensive understanding of how glow discharges may be used in analytical chemistry.

University of Wyoming
Laramie, Wyoming 82071

385. Solid Surface Luminescence Analysis
R.J. Hurtubise **$82,000**
Department of Chemistry

The main goal of this project is to develop a basic understanding of the physical and chemical interactions that enhance room-temperature fluorescence and room-temperature phosphorescence from organic compounds adsorbed on solid surfaces. Several spectral techniques are used to clarify the interactions. In addition, the effects of moisture, gases, and temperature on the fluorescence and phosphorescence quantum yields and the phosphorescence lifetimes of adsorbed compounds are investigated. A variety of luminescence parameters are calculated, such as triplet formation efficiencies and the rate constants for phosphorescence. Results will help to determine whether the luminescent molecules are held rigidly or if the solid matrix prevents collisions with oxygen, water, or impurity molecules. Other work involves the use of cyclodextrins to induce room-temperature luminescence from adsorbed compounds, and the comparison of several solid materials for improving the selectivity and sensitivity of room-temperature luminescence.

Chemical Engineering Sciences

American University
Washington, District of Columbia 20016

386. Theory of Condensable Gases
J.A. White **$126,400**
Department of Physics

The project objective is to refine a new theory that calculates the thermodynamic gas, liquid, and supercritical properties and phase diagrams of condensable gases. The theory takes into account the shortness of the range of attractive intermolecular forces in real gases and the enhanced fluctuations at all wavelengths that result. The fluctuations contribute 10 to 30% of the total pressure at many temperatures and densities. This large contribution from fluctuations is currently estimated only crudely and unreliably using empirical formulas to amend mean field theories or to interpolate between laboratory values found in measurements. The new theory has been found in tests against measurements performed for several gases to make predictions with order of magnitude improvement in accuracy compared with predictions made using existing mean field theories. The theory also makes correct predictions at the critical point as well as elsewhere on the gas–liquid phase diagram. We will further test the theory and use it to produce tabulations of thermodynamic properties of condensable gases for use where measurements are unavailable, unreliable, or insufficiently accurate.

Brigham Young University
Provo, Utah 84602

387. Thermodynamic Study of CO_2–Organic Compound Interaction at High Pressures and Temperatures
J.J. Christensen, R.M. Izatt **$81,000**
Department of Chemical Engineering

The primary objective of this project is to develop an understanding of how an additive affects the behavior of a supercritical mixture of CO_2 and freons with selected organic compounds under temperature-pressure conditions where either one or more of the components is in its supercritical region. The quantities measured are heats of mixing (H^E) of binary mixtures using flow calorimeters. The temperature and pressure ranges covered are 285 to 673 K and 8 to 12.5 MPa, respectively. The data allow evaluation to be made of the effect of temperature and pressure on the magnitude of H^E and on phase splitting. The occurrence of phase splitting is detected by discontinuities in the H^E curves, and the phase compositions are calculated from the mole fraction values at the points of discontinuity. In the critical region, large variations in H^E are found with temperature, pressure, and component mole fraction. The large changes in H^E have been modeled successfully using the Andrews-Soave and other equations of state. The eventual goal is to elucidate the chemistry occurring in supercritical fluid processes.

University of California
Davis, California 95616

388. Statistical Modeling and Analysis of Chemically Reacting Turbulent Flows
H.A. Dwyer, W. Kollmann **$84,950**
Department of Mechanical Engineering

The project objective is to develop new turbulent closure models for variable density turbulent flow and turbulent diffusion flames. The methods used to accomplish these goals are (1) physical and mathematical modeling and (2) sensitivity analysis. The modeling techniques are built around statistical closure assumptions and the use of Monte Carlo simulations of turbulent flow processes. Previous research has centered on the turbulent diffusion flame, but a new effort on the turbulent boundary layer diffusion flame has been initiated. The boundary layer has a wide range of turbulent length and time scales, and offers a much more complete test of the models developed. Current research focuses on the following studies: (1) velocity PDF simulations of the turbulent boundary layer; (2) turbulent heat transfer in the boundary layer; (3) multiscalar PDF simulations of the wall diffusion flame; and (4) development of approximate PDF formulations including intermittancy.

University of California
Santa Barbara, California 93106

389. Reaction Enhancement of Heterogeneously Catalyzed Reactions by Concentration Forcing
R.G. Rinker **$167,000**
Department of Chemical and **(18 mo.)**
Nuclear Engineering

Experimental and theoretical studies are under way to examine the behavior of nonlinear reacting systems under conditions of forced concentration oscillations. Compared to steady-state operation, concentration forcing can provide higher time-averaged production rates, increased catalyst life, improved selectivity, and lower energy requirements. This study focuses on the synthesis reactions of ammonia, methanol, and methane, and is expected to provide new insight into how surface concentrations of reactants on catalysts can be manipulated under conditions of practical interest to kinetically accelerate the overall rate of conversion. At moderately high pressures (~4MPa) and at typical operating temperatures (650 to 750 K) in a plug-flow configuration, ammonia production rate is diminished (compared to optimal steady state) when the cycling operation is between pure hydrogen and nitrogen. This is because the catalyst deactivates reversibly in the presence of the pure species. When cycling between N_2–/H_2 mixtures with appropriate cycle times, cycle splits, and composition amplitudes, significant enhancements of ammonia production rate occur. Nitrogen storage in the bulk-phase of the iron catalyst influences the surface kinetics, but only indirectly. For methanol synthesis from CO and H_2, a steady-state kinetic model has been developed and contains only five parameters (two of which are independently determined). The model includes the methanol contribution from CO_2, which stabilizes the catalyst against CH_4 production.

University of California/San Diego
La Jolla, California 92093

390. Premixed Turbulent Combustion

P.A. Libby	**$78,270**
Department of Applied Mechanics and Engineering Sciences	**(18 mo.)**

This project involves two areas of research. The first is a continuation of studies that relate to premixed laminar flames. Focus is on cylindrical premixed laminar flames (i.e., flames with reactants approaching the flame radially) for transformation into products in a thin reaction zone and exiting along an axis of rotation. Such flames can generally involve an azimuthal velocity distribution and are believed to represent the behavior of pockets of products in premixed turbulent flames. The second area of research concerns a long-term study of premixed turbulent flames in counterflowing configurations involving one or two reactant streams or in a reactant stream flowing against a solid surface. These flames are the turbulent analog of the laminar flames proven so valuable in fundamental combustion studies, and are thus expected to yield corresponding insight into the effect of strain on turbulent flames. The present approach is to conduct a series of analyses of increasing complexity and accuracy starting with the standard gradient transport model, continuing with the standard K-epsilon method, and concluding with the full Bray-Moss-Libby model of premixed turbulent combustion. We presently use a model for the mean rate of creation of products, which assumes the laminar flamelets are only weakly strained. Future extensions can incorporate the effect of strain and extinction on the flamelets and can thus deal with ignition and extinction of premixed turbulent flames. The influence of variations in enthalpy on the behavior of these flames can be included. Experiments on these flames are being conducted at the University of California (Berkeley).

Clarkson University
Potsdam, New York 13676

391. Analysis and Computer Tools for Separation Processes Involving Nonideal Mixtures

A. Lucia	**$84,000**
Division of Research	**(18 mo.)**

Analysis can play an important role in the development of reliable computer tools for the simulation and design of separation processes. Previous analysis established uniqueness for single-stage flash processes involving homogeneous mixtures for a variety of specifications. New results have been developed using differential geometry that categorize solutions to multicomponent homogeneous distillations as unique or nonunique according to various column specification sets. Consequences of this analysis pertinent to the development of reliable computer tools are currently under investigation. Mathematical analysis has been used to explain the multiplicity of vapor–liquid solutions to heterogeneous flash problems and the path connectedness of these solutions. Vapor–liquid–liquid solutions have proven to be unique using pair-wise vapor–liquid equilibrium and geometric methods. Based on this analysis, a new global method for solving three-phase flash problems that is reliable and efficient has been developed. Numerical experiments for three-phase distillations show very complex solution geometry. An understanding of factors that cause difficulties for current computer tools used for the simulation and design of three-phase distillations has been developed. Related mathematical analysis is under way.

Colorado State University
Fort Collins, Colorado 80523

392. Study of Improved Methods for Predicting Chemical Equilibria

T.G. Lenz	**$122,000**
Department of Agriculture and Chemical Engineering	**(18 mo.)**

The goal of this project is to develop improved techniques for predicting condensed-phase chemical equilibria. Current experimental studies seek to delineate intramolecular bond strain and substituent rotational and vibrational contributions to Diels-Alder reaction ΔH^0 and ΔS^0, using substituted anthracenes and maleic anhydrides at dilute concentrations in nonaqueous solvents. Experimental results are being used to develop and test modified force-field models for calculating thermodynamic properties for reactant and product molecules. The computational models are presently being applied to the Diels-Alder condensation of cyclopentadiene, for which considerable literature data are available for both gas and liquid phase equilibria. The full computational model will incorporate UNIFAC techniques for estimating activity coefficients. Both the force-field model for estimating gas-phase thermochemical properties and the UNIFAC solution activity coefficient model have separately proven reliable and generally applicable. Our objective is to couple force-field and UNIFAC techniques to provide a potentially powerful tool for predicting condensed-phase chemical equilibria for a wide variety of reactions of practical interest.

Columbia University
New York, New York 10027

393. Interaction of Turbulence and Chemical Reactions

R. Chevray	**$120,000**
Department of Mechanical Engineering	**(17 mo.)**

Flow in a two-dimensional mixing layer is utilized to study a well-known reaction with simple kinetic scheme. The flow represents a well-defined turbulent situation, and additional complexities of finite heat release are avoided by use of small concentrations for the reaction chosen ($NO + O_3 \rightarrow NO_2^* + O_2 \rightarrow NO_2 + h\nu + O_2$). Large Reynolds numbers, small dilution numbers, large reaction speed numbers, and several concentration rations are investigated. Conditional and conventional measurements have been made of mean and fluctuating quantities for both the velocity and concentration fields by laser Doppler anemometry and fiber optics absorption spectroscopy, respectively. Simultaneous cinefilm recording has been conducted to determine the convection velocity of the interface and hence the entrainment. Numerical simulation is set up to model directly the equations describing the evolution of the species concentration in the shear layer. We are presently investigating the role of chemical reaction on the turbulence itself by using higher concentrations, thus releasing heat, which introduces a buoyancy force. Measurements similar to the aforementioned ones will be made for this nonisothermal case.

Cornell University
Ithaca, New York 14853-5201

394. Experimental and Theoretical Studies of Dense Fluid Mixtures

W.B. Streett **$122,000**
School of Chemical Engineering **(18 mo.)**

The primary goals of this research are: (1) to carry out wide-ranging thermophysical property measurements for pure fluids and mixtures and (2) to develop improved methods for correlating, extrapolating, and predicting dense fluid properties using statistical mechanics and intermolecular potential theory. Recently completed experimental research includes measurements of the PVT properties of CF_4, CHF_3, and CCl_4 at pressures to 1,000 bars. Recent studies of CCl_4 are the first to use the redesigned and reconstructed, direct-weighing PVT apparatus and the new velocity-of-sound apparatus for dense fluids. The direct-weighing apparatus is designed to work from room temperature to 600°C and from 0 to 2,000 bars, and the velocity-of-sound apparatus is designed for work from -150 to 250°C and from 0 to 4,000 bars. Measurements are in progress on normal- and neopentane. Theoretical work has included applying various equations of state to the PVT data on CF_4 and CHF_3 to test the applicability of different kinds of equations of state to fluid data covering a wide range of conditions. A new form of the Tait equation of state for liquids has been developed to give an accurate description of the data for CCl_4.

University of Delaware
Newark, Delaware 19716

395. The Generalized van der Waals Theory of Pure Fluids and Mixtures

S.I. Sandler **$55,190**
Department of Chemical Engineering

The generalized van der Waals theory provides an excellent framework for understanding the basis for applied thermodynamic models currently in use and deriving new, improved models with potential application to heavy oils, coal liquids, and other synthetic fuels. Using a form of the generalized van der Waals partition function that we developed, we now understand the molecular-level assumptions explicit or implied in current thermodynamic models. Further, using computer simulation and integral equation theory, we can test these assumptions, establishing the theoretical validity of some and errors in others, especially some of the recently proposed local composition models. We can also make significant improvements in several models using the combination of the generalized van der Waals theory, integral equation theory, and computer simulation. Work focuses on developing new equations of state, mixing rules, and activity coefficient models for mixtures of molecules of widely differing size and functionality. An important feature of these models will be their firm theoretical basis and broad range of validity.

University of Florida
Gainesville, Florida 32611

396. Theoretical and Experimental Investigations of Fluctuation Thermodynamic Properties of Liquid Solutions

J.P. O'Connell **$85,000**
Department of Chemical Engineering

Fluctuation theory is being developed for analysis and application to strongly nonideal liquid mixtures including electrolytes. The objectives are (1) to complete a theoretical basis for properties of liquids that is rigorous and leads to useful correlations and (2) to establish a formulation and a data base for use in sensitive comparisons with models for strongly nonideal liquids. The results should be applicable to process design for energy-related processes including fossil fuel recovery, high-pressure reaction and separation systems (e.g., coal conversion, petrochemical hydrogenation), energy storage devices, extraction and crystallization (e.g., hydrometallurgy), industrial waste processing, and geologic systems for geothermal power production and mining. Results include (1) an analysis that provides correct expressions for electrostatic effects on all solution thermodynamic properties, (2) a statistical mechanical model for densities and activities of fully ionized salts in water up to high concentrations, (3) correlations for pressure effects on liquid volumes over wide ranges of every type of substance, (4) partial molar volumes at infinite dilution of salts in water to high pressures and temperatures, (5) binary ultracentrifuge sedimentation data for nonidealities at low concentrations, and (6) a data base of fluctuation solution properties for a variety of systems.

University of Illinois
Chicago, Illinois 60680

397. Development of the Analytic Variational Inequality Minimization (VIM) Equation of State

G.A. Mansoori **$99,000**
Department of Chemical Engineering **(18 mo.)**

This research concerns the development of an analytic equation of state for polar, quantum, and associated fluids and for fluid mixtures of practical interest. The approach is based on the variational inequality minimization (VIM) theory of statistical mechanics. The objectives of this research include the following: (1) extension of the VIM equation of state to pure fluids of polar and associated molecules due to hydrogen bonding; (2) extension of the applicability of the VIM equation of state to quantum fluids; (3) calculation of a set of intermolecular potential energy parameters based on the VIM theory for use in the VIM equation of state; and (4) extension of the VIM equation of state to mixtures.

398. Evaluation of Mixing Rules for Viscosity and Thermal Conductivity Using Nonequilibrium Molecular Dynamics

S. Murad **$88,000**
Department of Chemical Engineering **(18 mo.)**

The most commonly used methods for predicting viscosity and thermal conductivity of mixtures are based on solution theories. These theories enable the modeling of mixtures as hypothetical pure fluids or mixtures with few components (usually two) via mixing rules. Several mixing rules have been developed in the past few decades, but there is considerable disagreement in the scientific and engineering community regarding the accuracy of these mixing rules. The project objective is to examine the accuracy of these mixing rules by comparing them with exact computer simulation results, using nonequilibrium molecular dynamics (NEMD). Our studies will initially be based on mixtures modeled by the Lennard-Jones (LJ) intermolecular potential models. Most currently used theories are based upon or extrapolated from fluids that are well described using the LJ potential. The conclusions from our studies will therefore be quite general. For viscosity we plan to use time-varying oblique boundary conditions with homogeneous shear NEMD. For thermal conductivity we will use the noncanonical linear response theory. We will also examine the potential usefulness of group contribution methods in calculating transport properties of pure fluids and mixtures.

Johns Hopkins University
Baltimore, Maryland 21218

399. Prediction of Thermodynamic Properties of Coal Derivatives

M.D. Donohue **$123,000**
Department of Chemical Engineering

The purpose of this project is to develop an equation of state to predict the thermodynamic properties of coal derivatives. The equation is based on perturbed hard-chain theory, but includes additional terms for multipole interactions. The equation allows prediction of vapor pressures, densities, and solubilities for a wide range of organic molecules including multiringed aromatics. Pure component and mixture parameters are determined from experimental data when available; a group-contribution correlation is being developed to allow prediction of parameters for systems where no experimental data are available. The applicability of the new equation to supercritical fluid extraction is being studied. Hydrogen-bonding effects are taken into account to predict properties of systems containing H_2O, alcohol, and so forth. High-pressure vapor–liquid equilibrium measurements for CO_2–aromatic binary mixtures are made.

Louisiana State University
Baton Rouge, Louisiana 70803-7303

400. Molecular Dynamics Studies of Aromatic Hydrocarbon Liquids

E. McLaughlin **$74,410**
Department of Chemical Engineering **(18 mo.)**

This research is concerned with the molecular dynamics investigation of aromatic hydrocarbon liquids and their mixtures. Focus is on the simulation of aromatic mixtures encountered in dense coal-derived chemicals, such as naphthalene and phenanthrene, in aromatic solvents such as benzene and toluene. Previous computer simulations have been limited to atomic and molecular fluids and their mixtures. The objective is to develop predictive models for determining the properties of complex aromatic liquids encountered in heavy crudes and/or coal processing.

Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

401. Thermodynamics and Rate of Methanol Conversion to Hydrocarbon on Zeolites

R.A. Alberty **$128,000**
Department of Chemistry **(16 mo.)**

The objective of this project is to determine the extent to which thermodynamics can account for the distribution of products in the gasoline produced from methanol using zeolite catalysts, and the way in which deviations from equilibrium can be accounted for in terms of rate constants. These calculations are made using isomer groups and linear restrictions in a general equilibrium program. Calculations are made for various temperatures, pressures, catalyst selectivity, and extent of reaction. In order to make these calculations, tables of isomer group thermodynamic properties are produced, and the Benson method is used to augment literature data. Thermodynamic data on higher isomer groups are obtained by linear extrapolation. New methods for making chemical equilibrium calculations using homologous series groups and continuous thermodynamics are being developed. Since the polymerization of alkenes by zeolite catalysts in the range of 450 to 800 K may approach equilibrium, the equilibrium distributions of isomer groups have been calculated as a function of temperature, pressure, and selectivity. The rate equations for this polymerization up to $C_{13}H_{26}$ have been integrated using the fourth order Runge-Kutta method on the basis of two assumptions about the rate constants. This makes it possible to explore the effects of temperature, pressure, and selectivity on the kinetics as well.

National Bureau of Standards
Boulder, Colorado 80303

402. Integrated Theoretical and Experimental Study of the Thermophysical Properties of Fluid Mixtures

W.M. Haynes **$233,000**
Thermophysics Divison

The primary goals of this project are (1) to increase basic understanding of the behavior and properties of complex fluid mixtures with advances in theory, (2) to develop predictive procedures for the properties of fluids and fluid mixtures, and (3) to obtain carefully selected experimental data to support theoretical and modeling efforts. Recent PVT measurements on toluene, phase-equilibria data for R-13 + butane and methanol + water mixtures, and heat-of-mixing data for toluene + benzene mixtures have resulted in improvements in modeling the behavior of complex reacting systems. Current studies include: (1) theoretical development of the field space corresponding states model with improved mixing rules based on microscopic theory, with emphasis on mixtures containing species that exhibit large differences in size, shape, and/or polarity; (2) computer simulation studies of fluids under shear, to obtain information on the structure of liquids; (3) a theoretical model that represents the phase behavior of near-critical fluid mixtures in terms of field variables; (4) a transport property theoretical model consistent with the experimentally observed critical enhancement in the thermal conductivity of mixtures; (5) a heat of mixing study investigating hydrogen bonding (association) in five-membered ring compounds; and

(6) a statistical thermodynamic model that describes the phase behavior or partitioning of two-phase polymer + polymer + water systems.

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

403. *Thermodynamic Characterization of Condensed-Ring Compounds*

M.M. Strube	**$285,000**
Processing and Thermodynamics Division	**(15 mo.)**

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

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

404. *Theoretical Studies of Multicomponent Mixtures: Phase Equilibrium and Transport*

J.M. Kincaid	**$100,000**
Department of Chemistry	**(16 mo.)**

The purpose of this research is to develop methods for characterizing the thermodynamic and transport properties of multicomponent fluids. The fluids may consist of a finite number, a countable infinity, or a continuum of chemical species. The principal objective is to develop methods to describe multicomponent phase equilibrium (i.e., the solution of phase equilibrium conditions). A second objective is to derive a nonequilibrium description of continuous mixtures and to calculate their transport properties. Recent progress includes: (1) a thermodynamic perturbation theory for multicomponent and continuous mixtures applied to the solution of equilibrium and critical-point conditions; and (2) a thorough study of thermal diffusion in binary and ternary hard-sphere mixtures.

405. *Thermophysical Properties of Multiphase Systems*

G.R. Stell	**$55,000**
Department of Chemistry	**(9 mo.)**

Ongoing research to obtain the transport properties of fluids and fluid mixtures in analytically tractable form has continued. Two general approaches have been used. The first is a conditional-probability approach that yields a description of solvent–solute collision involving reduced mass and collision diameter renormalized by the presence of the solvent background. In the limit of identical solute and solvent particles, this results in a new pure-fluid theory as well. A second general approach is information theoretic, based on the maximization of entropy subject to increasingly refined constraints. This yields a sequence of successively more refined versions of a kinetic variational theory. When the pair potential includes a hard-sphere reference-potential term, the theory can be further improved by insertion of an improved treatment of the correlation induced by core–core collisions, yielding a sequence of kinetic reference theories. A study of the thermophysical properties of multisolvent ionic fluids has also been initiated. This includes study of the so-called Donnan problem, relating concentrations, membrane potential, and osmotic pressure, which offers a powerful tool for studying colloidal systems via determination of membrane potentials.

University of Pennsylvania
Philadelphia, Pennsylvania 19104

406. *Thermodynamics of Systems of Very Many Components*

E.D. Glandt	**$174,500**
Department of Chemical Engineering	**(33 mo.)**

This theoretical and computational project deals with thermodynamic and structural behavior of polydisperse fluid mixtures such as liquid fuels and polymer solutions and melts. The continuous Lennard-Jones model substance is an appropriate first representation of the former. A perturbation theory was developed for narrow cuts, while Monte Carlo computer simulations are the approach chosen to test the theory and to describe the properties of very wide distributions like those encountered in reservoir modeling and in crude liquids in general. A very important aspect of phase equilibrium involving wide distributions is the prediction of the dew point, as it is affected by the presence of a tail of heavy components. Accordingly, the focus of these simulations is the calculation of distributions of the activity coefficients. A generalization of Widom's average potential theory specific to the polydisperse case was developed and is being compared with existing techniques.

Princeton University
Princeton, New Jersey 08544

407. *Anisotropy, Charge Distribution, and the Properties of Dense CO_2: Molecular Dynamics Studies*

P.G. Debenedetti	**$65,000**
Department of Chemical Engineering	**(18 mo.)**

This project involves a fundamental study of the relationship between carbon dioxide's anisotropy (i.e., nonsphericity) and charge distribution and its pure component properties over a number of different state points, including the liquid and supercritical regions. Emphasis is on transport and nonequilibrium behavior. Equilibrium and structural properties are also included. This work is to enhance our understanding of the behavior of carbon dioxide from a molecular perspective, thereby providing a sound scientific base upon which engineering generalizations and correlations can be built.

Purdue University Research Foundation
West Lafayette, Indiana 47907

408. Gas–Liquid–Liquid Equilibria in Mixtures of Water, Light Gases, and Hydrocarbons

K.-C. Chao, H.M. Lin **$110,000**
School of Chemical Engineering **(18 mo.)**

Phase equilibrium in mixtures of water + light gases, and water + heavy hydrocarbons has been investigated with the development of new modeling equations and new experimental data. Models of local composition have been developed from computer-simulated square-well fluids to express segregation of molecules in fluid mixtures. One local composition model has been used with the Cubic-Chain-of-Rotators, the Soave, and the Peneloux-Rauzy equation of state to improve either dramatically or significantly the description of phase equilibria in mixtures of water and mixtures of polar substances in general. A model for the coordination number of square-well molecules has been obtained from the Monte Carlo simulation. A model for coordination number is fundamental for deriving equation of state. The equation of state will apply directly to mixtures, and contain local composition as an integral part of its structure. A new equation of state is obtained by combining the accurate Keenan and Keys equation for steam and the accurate BACK equation for light gases and hydrocarbons using the results of Jorgensen and coworkers on the structure of water. The new equation effectively interpolates between the two accurate equations for the calculation of mixtures of water, and by extension to polar substances and their mixtures in general. Liquid–liquid equilibrium has been determined experimentally for six binary mixtures of water + a heavy hydrocarbon or a hydrocarbon derivative. A new visual equilibrium cell has been designed and made for experiments at pressures up to about 60 MPa.

Stanford University
Stanford, California 94305

409. Fundamental Studies of Heat Transport, Fluid Mechanics, and Stability in Porous Media

G.M. Homsy **$130,240**
Department of Chemical Engineering

This project treats problems in flow and transport phenomena in porous media whose solutions are of interest in energy recovery processes. Macroscopic and microscopic problems are addressed. We have recently focused on viscously driven instabilities (fingering) that occur in displacement processes. For immiscible flows, we have discovered an intriguing tip-splitting instability of large-scale fingers that may, under some circumstances, lead to geometrically complex fractal patterns. Experimental work continues. We have recently completed a linear theory of fingering in miscible displacements that is in excellent agreement with available experiments, and we have indicated important effects of areal spreading on stability. Current work is extending this theory to nonlinear fingering via direct numerical simulation. Evidence is now accumulating for tip splitting in miscible displacements at high Peclet numbers.

University of Wisconsin
Madison, Wisconsin 53706

410. Interphase Transport and Multistage Separations

W.E. Stewart **$135,000**
Department of Chemical Engineering **(18 mo.)**

The project goal is to provide new physical understanding of stagewise separation processes, and efficient algorithms for computer-aided engineering of these processes. The physical studies include boundary-layer analysis and multicomponent transport theory; the algorithmic studies include new collocation and continuation methods. Recent results include: (1) asymptotic expansions for entry-region heat and mass transfer in laminar and turbulent boundary layers; (2) a comprehensive numerical study of matrix methods and corresponding reference-property rules for multicomponent mass transfer computation in variable-property systems; and (3) adaptive finite-element collocation strategies for robust analysis of multistage separations in the presence of steep fronts or more than one liquid phase.

Heavy Element Chemistry

Florida State University
Tallahassee, Florida 32306

411. Research in Actinide Chemistry

G.R. Choppin **$102,000**
Department of Chemistry

Complexation thermodynamics, redox kinetics, and solvent extraction are the primary areas of research on systems that may increase our fundamental understanding of actinide element behavior, particularly in separation schemes and in ecosystems. The trivalent lanthanides are studied as models of actinide behavior, using a broader variety of techniques than feasible for the radioactive actinides. Emphasis has been given to interaction of these metals with organic ligands, partially for modeling the behavior of actinides with organic compounds in the environment (e.g., in groundwaters of potential waste repository sites). Study of alkyl and aromatic carboxylates has provided insight into the effect on complexation stability of chelate ring size and electronic charge transfer via resonance and inductive effects. Study of simple model ligands has aided the understanding of actinide binding to polyelectrolytes, such as humic materials found in groundwaters and soils. Humic material readily reduced PuO_2^{+2} species to Pu^{+4}. Our studies suggest that the phenol groups are responsible; research is in progress on reduction of NpO_2^{+2} and PuO_2^{+2} by hydroxy and phenolic compounds. Milligram amounts of ^{248}Cm have been used in calorimetric studies to obtain the first directly measured complexation enthalpic data for this element. The synergic solvent extraction of actinides has been measured via calorimetric titration (e.g., $Th(TTA)_4$ + TBP) in benzene. The importance of the role of hydrate water in these systems is obvious from the thermodynamic data.

University of New Mexico
Albuquerque, New Mexico 87131

412. Development of Surface Immobilized Ligands for Actinide Separations

R.T. Paine **$65,000**
Department of Chemistry

The project objective is to develop systematic synthetic methods for the formation of new classes of organic solvent-soluble extractants and for the production of solid-state immobilized extractants suitable for selective chromatographic separations of metal ions present in nuclear fuel reprocessing and industrial waste solutions. In particular, fundamental investigations of steric and electronic effects that influence and modify extractant–metal ion interactions are in progress, and new flexible bifunctional and trifunctional phosphonate extractants are prepared. Isolated liquid–liquid extraction complexes of these ligands are studied at the molecular level by spectroscopic and x-ray crystallographic methods. In turn, the resulting molecular architecture data are used to design improved extractants and to model surface immobilized extractant–metal interactions. Extraction equilibria for lanthanide and actinide ions in contact with several phosphonate extractants attached to various organic and inorganic polymer backbones are measured.

Ohio State University
Columbus, Ohio 43210

413. Molecular Orbital Studies of the Bonding in Heavy-Element Organometallics

B.E. Bursten **$46,290**
Department of Chemistry

Our previous research has established the $X\alpha$–SW molecular orbital method with quasi-relativistic corrections as a viable electronic structure tool for the study of organoactinide systems. We have initiated molecular orbital investigations into several aspects of organoactinide chemistry. The comparative bonding capability of small molecule substrates such as carbon monoxide, phosphines, or isonitriles is under way through an investigation of the U(III) systems $(\eta^5\text{-}C_5H_5)_3UL$. These studies are closely related to our previous ones on U(IV) and Th(IV) organometallics, and will also relate to calculations on model systems that contain uranium-to-carbon and uranium-to-nitrogen multiple bonds. Recent reports of molecules containing direct metal–metal bonds between an actinide metal and a transition metal have led to several questions concerning the comparative roles of the actinide 5f and 6d orbitals in the metal–metal bonding. We are investigating these through calculations on molecules containing unsupported metal–metal bonds, such as $(\eta^5\text{-}C_5H_5)_2Th(X)\text{–}Ru(\eta^5\text{-}C_5H_5)(CO)_2$. We are using our calculations to investigate the electronic structural constraints on the synthesis of molecules that contain direct multiple bonds between two actinide centers. Calculations on hypothetical molecules such as $U_2(CH_3)_6$ are indicating possible routes to the design of ligand systems that will be capable of supporting direct uranium–uranium bonds.

SRI International
Menlo Park, California 94025

414. Chemistry of Gaseous Lower Valent Actinide Halides

D.L. Hildenbrand, K.H. Lau **$115,970**
Physical Sciences Division

The objective of this project is to provide accurate thermochemical information for key actinide halide, oxyhalide, and related systems, starting with uranium halides, so that the basic factors underlying the chemical bonding and chemical reactivity in these systems can be elucidated in a systematic way. Our principal focus is on the gaseous halides, mainly the lower valent halides, since there is little or no thermodynamic or spectroscopic information on these species. Bond dissociation energy and absolute entropy data are derived from chemical equilibrium measurements made primarily by high-temperature mass spectrometry. The bond dissociation energies and their variation with the number of halogen ligands yield insight into the electronic character of the bonding, while the absolute entropies provide useful checks on assigned structures and electronic partition functions. Current studies are concerned with the gaseous thorium–iodine system, the lower valent uranium oxyfluorides and oxychlorides, and the thorium oxychlorides. A clear pattern of bond dissociation energies and electronic entropies is beginning to emerge; these patterns will be useful in modeling the thermochemistry of the heavier actinide halides, which will be much more difficult to study.

University of Tennessee
Knoxville, Tennessee 37996-1200

415. Magnetic Measurements of the Transuranium Elements

S.E. Nave **$97,000**
Department of Physics and Astronomy

A SQUID-based micromagnetic susceptometer in the facilities at the Transuranium Research Laboratory is used to measure the magnetic properties of americium, curium, berkelium, californium, and einsteinium metals, alloys, and compounds. The research catalogs magnetic behavior of unmeasured heavy actinides between 4.2 K and room temperature and 0 to 5 tesla. The study provides a measure of the degree of localization of the 5f electrons and examines the effects produced by neighbor–neighbor overlap. The effective magnetic moments of heavy atoms and the observed magnetic transition temperatures (if any) are examined within the context of the intermediate coupling model. A technique has been developed to grow single crystals of actinide trihalides with masses in the range 1 microgram to 1 milligram without loss of material. Magnetic measurements on multimicrogram-size single crystals of $CfCl_3$ as a function of orientation have allowed a determination of its magnetic anisotropy. These measurements have provided an additional constraint on crystal-field parameters within the framework of a crystal-field model including intermediate coupling effects.

416. Physical-Chemical Studies of the Transuranium Elements

J.R. Peterson **$137,000**
Department of Chemistry

This project provides training for pre- and postdoctoral students in chemical research with the transuranium elements through continuing investigations of the basic chemical and physical properties of this group of elements and the interpretation and correlation of the results obtained. New knowledge is being accumulated in the following areas: (1) the role of the 5f electrons in the bonding in actinide elements and compounds; (2) the relationships of metallic structures to metallic valence and radius; (3) the extent and magnitude of the actinide contraction; (4) the magnetic, thermodynamic, spectroscopic, and crystallographic properties of these materials as related to general theories; (5) the effect of self-irradiation on chemical and physical properties; (6) the chemical and physical consequences of radioactive decay in the bulk-phase solid state; and (7) in general, the range of validity of the actinide hypothesis. Research activities include: (1) spectroelectrochemical studies in aqueous and nonaqueous media; (2) measurement of heats of solution; (3) absorption and Raman spectroscopies in solution and in the solid state (the latter as a function of temperature or pressure); (4) structural changes of transuranium elements and compounds as a function of temperature or pressure; (5) direct or indirect (via radioactive decay) synthesis of compounds containing unusual oxidation states; (6) determination of the structures of einsteinium compounds; and (7) studies of the fundamental chemistry of the transeinsteinium elements.

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. Iran Thomas, Director of Materials Sciences, ER-13, U. S. Department of Energy, Washington, D.C. 20545.

ATOMIC SPECTROSCOPY FACILITY

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

The Argonne spectroscopic facility is designed for high-resolution investigations of the spectroscopic and dynamic properties of atomic and molecular systems. A unique combination of large-scale dispersive instruments with state-of-the-art holographic gratings and pulsed, single-mode, tunable light sources are available. Diode-array and standard detectors are directly interfaced to micro-computers for control of experiments and pulse-to-pulse normalization of signals which result from multi-photon excitation processes. A pulsed molecular beam apparatus equipped with a time-of-flight spectrometer is available to produce low temperature molecular species. Nd-YAG and excimer lasers are available to pump dye oscillators and amplifiers. Their output is used with frequency doublers and sum frequency generators to cover the 200 to 850 nm spectral region. The four-wave mixing process in metal vapors and rare gases is used to produce coherent radiation between 118 and 200 nm.

COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists.

PERSON TO CONTACT FOR INFORMATION

J. P. Hessler
Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Phone:
Comm. (312) 972-3717
or FTS 972-3717

TECHNICAL DATA

Resolving power	
30-foot Paschen-Runge spectrograph	$>5 \times 10^5$
5-meter Czerny-Turner spectrograph	$>10^6$
Tunable dye lasers	$>10^6$
Vacuum-ultraviolet coherent source	$>10^6$

Wavelength range, nm	
30-foot Paschen-Runge spectrograph	200 to 900
5-meter Czerny-Turner spectrograph	120 to 500
Tunable dye lasers	200 to 850
Vacuum-ultraviolet coherent source	118 to 200

4.5-MV DYNAMITRON ACCELERATOR

Physics Division
Argonne National Laboratory
Argonne, IL 60439

The Argonne Physics Division operates a high-current 4.5-MV Dynamitron accelerator which delivers magnetically analyzed beams of most atomic ions and many molecular ions. Among the unique facilities associated with the Dynamitron are (1) a beam line capable of providing "supercollimated" ion beams that permit angular measurements to accuracies of 0.1 mrad, (2) a beam-foil measurement system capable of measuring lifetimes to a few tenths of a nanosecond, (3) a 28-inch-diameter general-purpose scattering chamber, (4) a laser-ion beams system where an argon pumped dye laser beam is coaxial with the ion beam, (5) a variety of electron spectrometers including a high-resolution, large solid-angle McPherson spherical analyzer, (6) a large area multiwire proportional counter capable of detecting up to eight particles simultaneously with submillimeter position and subnanosecond time resolution, and (7) a post-acceleration chopper system giving beam pulses with widths that can be varied from 1 nsec to several msec at repetition rates variable up to 8 MHz. A VAX 11/750 computer system with direct links to Argonne's central computing facility is used for on-line data acquisition, analysis, and the control of experiments.

COLLABORATIVE USE

Visiting scientists use the accelerator either in collaboration with Argonne investigators or as independent groups.

PERSON TO CONTACT FOR INFORMATION

E. P. Kanter
Physics Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Phone:
Comm. (312) 972-4050
or FTS 972-4050

TECHNICAL DATA

Range of terminal voltages attainable	0.3 to 4.8 MV
Range of ion beam currents attainable	10 aA to 500 μA
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 = 0,5), $C_2H_n^+$, $C_3H_n^+$, OH_n^+ (n = 1,3), CO^+, O_2^+, etc.
Pulse mode (post-chopper)	
Pulse width	1 nsec to 10 msec
Repetition rate	1 MHz to 8 MHz

PREMIUM COAL SAMPLE PROGRAM

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

The purpose of the Premium Coal Sample Program is to provide the coal science research community with long-term supplies of a small number of premium coal samples that can be used as standards for comparison. The premium coal samples produced from each coal and distributed through this program are as chemically and physically identical as possible, have well-characterized chemical and physical properties, and are stable over long periods of time. Coals were mined, transported, processed into the desired particle and sample sizes, and packaged in environments as free of oxygen as possible while maintaining the natural moisture content in order to ensure that the coals will be in as pristine and stable a condition as possible.

AVAILABILITY

The first samples became available in mid-1985, and the set of eight samples was completed in early 1987. These samples are available to research personnel at a nominal replacement cost. A very limited quantity of lump coal, stored under similar inert conditions, is available on special request for special physical property measurements. Distribution of these samples will be guided by policies established with the help of a users advisory committee. The processing facility may be available for occasional processing of special samples.

PERSON TO CONTACT FOR INFORMATION

Dr. Karl S. Vorres
Chemistry Division, Bldg. 211
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Phone:
Comm. (312) 972-7374
or FTS 972-7374
Telex:
TWX 910-258-3285
USDOE-CH ARGN

PULSE RADIOLYSIS FACILITY

Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

The Argonne linear electron accelerator was designed for chemical research. The moderate energy of the electron accelerator (maximum energies of 21 MeV transient mode, 14 MeV steady state) allows the use of the electron beam for the generation of transient species without nuclear activation. The pulse width can be varied from 25 psec to 10 μsec. In addition, a 5 psec pulse with the same peak current has been developed. In liquids, transient concentrations up to 20 μM can be generated with the 25-psec pulse, and concentrations in excess of 10 mM can be generated with the longest pulse. Instrumentation for measurement of chemical processes allows kinetic spectrophotometric absorption and emission and fast conductivity measurements. Simultaneous multiwavelength kinetic spectrophotometric measurements are possible, and very high time resolution measurements that use the short pulse capability of the linac can also be made, both in absorption and emission. All data acquisition equipment is computer interfaced to provide accurate data reduction. Sample preparation and handling facilities are available for solid, liquid, and gaseous samples.

COLLABORATIVE USE

Collaborative experiments can be arranged with appropriate staff scientists.

PERSON TO CONTACT FOR INFORMATION

Charles D. Jonah
Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Phone:
Comm. (312) 972-3471
or FTS 972-3471

TECHNICAL DATA

Energy		
Transient mode	21 MeV	
Steady-state mode	14 MeV	
Average current	200 μA (maximum)	
Pulse repetition rate	Single pulse to 800 pps (800 pps not possible for all pulses)	
Current/pulse		
Transient mode	20 A peak	
Steady-state mode	1.5 A peak	
Picosecond pulse	25 nC (charge per pulse)	
Piosecond (5 ps)	7 nC	
Pulse width	5 ps	transient mode
	25 ps	
	4 to 100 ns	
	.15 to 10 μs	steady state mode

ATOMIC PHYSICS AND NUCLEAR ANALYTICAL TECHNIQUES

Atomic and Applied Physics Division
Department of Applied Science
Brookhaven National Laboratory
Upton, NY 11973

The objective of this program is to make available facilities for research in atomic physics and the development and application of nuclear analytical techniques. Experiments in these fields require the availability of a wide range of ion and photon beams for maximum effectiveness. These beams cannot be provided at a single accelerator, but require the use of varied apparatus at a whole complex of accelerators. A 3.5-MV electrostatic accelerator is used primarily for experiments on nuclear analytical techniques. Notable features include a triton beam, medium resolution microprobe, rabbit system, and 200-kV ion implanter arranged for simultaneous implantation and analysis. The MP tandem accel-decel accelerator provides beams of most elements with an energy range from 2 MeV to 500 MeV. Ion charge state and ion energy can be selected over a wide range of energies using the accel-decel feature. Possible use of the tandem accelerators is determined by the needs of the relativistic heavy-ion program. Equipment for beam-foil spectroscopy and many types of ion-atom collision experiments are available. Photon beams with energies from 3 to 20 keV are provided at the National Synchrotron Light Source (NSLS). Either white or monochromatic radiation can be selected. The high brightness of the source gives unique opportunities in both atomic physics and nuclear analytical technique experiments. Extensive instrumentation is available in both areas.

COLLABORATIVE USE

These facilities are open for use by qualified scientists. Arrangements can be made for collaboration with Brookhaven scientists or for independent experiments. Proprietary use is possible on a full-cost recovery basis. In some cases a proposal for review by program advisory committees will be necessary.

PERSON TO CONTACT FOR INFORMATION

K. W. Jones
Division of Atomic and Applied Physics
Department of Applied Sciences
Building 901A
Brookhaven National Laboratory
Upton, NY 11973

Phone:
Comm. (516) 282-4588
or FTS 666-4588

TECHNICAL DATA

200-kV Ion Implanter	
Range of terminal voltages attainable	20 to 200 kV
Range of maximum ion beam currents available	1 to 100 μA
Ion beams available	Many elements
3.5-MV Electrostatic Accelerator	
Range of terminal voltages attainable	.3 to 3.5 MV
Range of maximum ion beam currents available	10 to 100 μA
Ion beams available	^{1}H, ^{2}H, ^{3}H, ^{3}He, ^{4}He, and heavier gaseous elements
Repetition rate	DC only
MP-Tandem Accel-Decel Accelerators	
Range of terminal voltages available	1 to 18 MV
Output currents	Up to 1 μA
Ion beams available	Most elements
Ion energy and charge state	Variable with accel-decel capability
Repetition rate	DC or pulsed with variable repetition rate
NSLS X-Ray Facility	
Photon energy range	Filtered white radiation
Photon flux at target	4×10^7 photons/(sec · eV · mm^2) at 8 keV

NATIONAL SYNCHROTRON LIGHT SOURCE

National Synchrotron Light Source
Brookhaven National Laboratory
Upton, NY 11973

The National Synchrotron Light Source (NSLS) is the nation's largest facility dedicated solely to the production of synchrotron radiation. The facility has two electron storage rings: a vacuum ultraviolet (VUV) ring which operates at an electron energy of 750 MeV designed for optimum radiation at energies between 10 eV and 1 keV, and an X-ray ring which operates at 2.5 GeV to optimize radiation between 1 KeV and 20 KeV. With each of the 30 X-ray and 17 VUV beam ports being further split into two to four beam lines it will be possible, when the NSLS becomes fully operational, to have as many as 100 experiments running simultaneously.

A total of six insertion devices will be installed on the X-ray and VUV rings. These devices, known as either wigglers or undulators, are special magnets which produce synchrotron radiation orders of magnitude brighter than is available from the conventional bending magnets. The insertion devices will be used for microscopy, medical research, materials sciences, spectroscopy, and Transverse Optical Klystron (TOK) experiments.

The NSLS is a facility where a wide range of research techniques are being used by biologists, chemists, solid state physicists, metallurgists, and engineers for basic and applied studies. Among the techniques are EXAFS (extended X-ray absorption fine structure), scattering, diffraction, topography, radiography, fluorescence, interferometry, gas phase spectroscopy, crystallography, photoemission, radiometry, lithography, microscopy, circular dichroism, photoabsorption, and infrared vibrational spectroscopy.

Proprietary research can be performed at the NSLS. The DOE has granted NSLS a Class Waiver under whose terms the Proprietary User is obligated to pay the full cost recovery rate for NSLS usage. In return, the user has the option to take title to any inventions made during the proprietary research program and to treat as proprietary all technical data generated during the proprietary research program.

USER MODES

The policy for experimental utilization of the NSLS is designed to enable the scientific community to cooperate in establishment of a comprehensive long-range experimental program. In addition to the beam lines constructed by the NSLS staff for general usage, a large number of beam lines have been designed and instrumented by Participating Research Teams (PRTs). The PRTs are entitled to up to 75% of their beam line(s) operational time for a three-year term. Insertion Device Teams (IDTs) have been formed to design, fabricate, commission, and use wiggler and undulator beam lines. The conditions and terms are similar to those of the PRTs.

General users are scientists interested in using existing NSLS facilities for experimental programs. They are scheduled by an independent beam time allocation committee for a percentage of operating time for each beam line. Liaison and utilization support is provided to the General User by the cognizant beam line.

A program is available to support faculty/student research groups performing experiments at the NSLS as General Users, or performing neutron experiments at the BNL High Flux Beam Reactor (HFBR). The program is designed to encourage new users to these facilities and defray expenses incurred during exploratory visits to BNL, and while conducting initial experiments at the NSLS and HFBR. It is aimed at university users having only limited grant support for their research.

PERSON TO CONTACT FOR INFORMATION

S. White-DePace
NSLS, Bldg. 725B
Brookhaven National Laboratory
Upton, NY 11973

Phone:
Comm. (516) 282-7114
or FTS 666-7114

TECHNICAL DATA

Facilities	Key features	Operating characteristics
VUV electron storage ring	High brightness; continuous wavelength ($\lambda > 5$ Å) 17 ports	0.75-GeV electron energy
X-ray electron storage ring	High brightness; continuous wavelength range ($\lambda > 0.5$ Å) 30 beam ports	2.5-GeV electron energy

Research area	Wavelength range (Å)	Number of instruments
Circular dichroism	1400 to 6000	1
Energy dispersive diffraction	0.5 to 2.5	2
EXAFS, NEXAFS, SEXAFS	0.3 to 120	25
Gas phase spectroscopy/ atomic physics	0.6 to 14.5	3
Infrared spectroscopy	2.5×10^4 to 1.2×10^7	2
Lithography/microscopy	0.6 to 70	5
Medical research	0.37	1
Nuclear physics	2.5×10^{-5} to 2.5×10^{-4}	1
Photoionization	0.6 to 12500	5
Radiometry		1
Reflectometry	7 to 6000	2
Research & development/ diagnostics	white beam	6
Time resolved fluorescence	1000 to 12500	2
Topography	0.3 to 3	3
Transverse optical klystron	12.5 to 1250	1
VUV & X-ray photoemission spectroscopy	0.3 to 1.5	26
X-ray crystallography	0.3 to 4	9
X-ray fluorescence	0.6 to 6000	3
X-ray scattering/ diffraction	0.3 to 6000	20

NUCLEAR ANALYTICAL TECHNIQUES

Atomic and Applied Physics Division
Department of Applied Science
Brookhaven National Laboratory
Upton, NY 11973

This program makes available facilities for the development and application of nuclear analytical techniques. A 3.5-MV electrostatic accelerator provides ion beams with currents of up to 100 μA with various gaseous species such as ^{1}H, ^{2}H, ^{3}H, ^{3}He, and ^{4}He. Notable features include a triton beam, medium resolution microprobe, rabbit system, and 200-kV ion implanter arranged for simultaneous implantation and analysis. Photon beams with energies from 3 to 20 keV are provided at the National Synchrotron Light Source (NSLS). Either white or monochromatic radiation can be selected. The high brightness of the source gives unique opportunities for analytical microprobe methods: determinations of elemental composition using fluorescence techniques are possible with spatial resolutions of ~10 μm and detection sensitivities of about 100 parts per billion (mass fraction). Applications in the geochemical, biomedical, and materials sciences are actively supported.

COLLABORATIVE USE

These facilities are open for use by qualified scientists. Arrangements can be made for collaboration with Brookhaven scientists or for independent experiments. Proprietary use is possible on a full-cost recovery basis. In some cases a proposal for review by program advisory committees will be necessary.

PERSON TO CONTACT FOR INFORMATION

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JAMES R. MACDONALD LABORATORY

Department of Physics
Kansas State University
Manhattan, KS 66506

Three accelerators are operated primarily for atomic physics research. These accelerators are a 6-MV EN-tandem accelerator, a 3-MV Van de Graaff, and a 100-kV accelerator. Either foil or gas poststripping between the 90° and the switching magnets is possible for tandem beams. Available experimental facilities include (1) a 4.5-meter flight tube for impact parameter measurements, (2) a curved crystal X-ray spectrometer, (3) spherical sector and cylindrical electron spectrometers, (4) hydrogen atom and metal vapor oven targets, (5) low-energy high-charge recoil ion sources, (6) a 45-inch diameter scattering chamber, and (7) Si(Li), proportional counter, avalanche, and channel-plate detectors. The laboratory is available to users who require the unique facilities of the laboratory for 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
James R. MacDonald Laboratory
Department of Physics
Kansas State University
Manhattan, KS 66506

Phone: (913) 532-6783

TECHNICAL DATA

EN Tandem

Beams	Most elements
Terminal voltages	0.3 to 6 MV
Output currents	Up to 10 μA, 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	^{1}H or ^{4}He
Terminal voltages	0.3 to 3 MV
Output currents	Up to 100 μA
Repetition rate	DC only
Magnet limitations	None

100-kV Accelerator

Beams	Most elements
Terminal voltages	20 to 100 kV
Output currents	Up to 10 μA, depending on the ion species
Magnet limitations	None

PULSE RADIOLYSIS FACILITY

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

The Notre Dame pulse radiolysis facility is based on a 5-nsec electron pulse from an 8-MeV linear accelerator. It is fully instrumented for computerized acquisition of optical and conductivity information on radiation chemical intermediates having lifetimes of 10 nsec and longer. An excimer laser/dye laser combination is available for use at the pulse radiolysis facility for double-pulse experiments involving photolysis of radiolytic transients. Energies of ~400 mJ at 308 nm and ~50 mJ at various near-UV and visible wavelengths are available. Detectors having response times of ~2 nsec are available. For typical optical absorption studies, where one produces $10^{-5}M$ of intermediates, spectral and kinetic information can be obtained on species having extinction coefficients in excess of 100 $M^{-1}cm^{-1}$. Conductometric methods in aqueous solution cover the pH range of 3 to 11. Data are recorded digitally and stored in magnetically readable form for rapid off-line examination of spectral and kinetic details.

COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists or by a proposal to the laboratory director.

PERSON TO CONTACT FOR INFORMATION

J. J. Bentley, Assistant Director
Notre Dame Radiation Laboratory
Notre Dame, IN 46556

Phone:
Comm. (219) 239-6117

TECHNICAL DATA

Electron source	8-MeV linear accelerator
Operating mode	Single pulse, with signal averaging
Data collection	LSI-II
Pulse width	5, 10, 20, 50 nsec
Time resolution (RC)	2 nsec
Pulse current	Up to 1 A
Repetition frequency	0.2 sec^{-1}
Optical absorption measurements	
Spectral region	210 to 750 nm
Sensitivity	±0.00002 absorbance
Conductivity	
pH range	3 to 11
Sensitivity	±5 mhos/cm

ELECTROMAGNETIC ISOTOPE SEPARATIONS (CALUTRON) FACILITY

Operations Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

The objective of this facility is to separate and provide multigram quantities of highly enriched separated stable and selected radioactive isotopes, including the actinides, to the research community. Important aspects of the program are process improvement, demonstration of cost-effective methods of isotope enrichment, and chemical recovery procedures. All isotopically enriched samples are distributed through a regular sales program or are circulated to the research community on a loan basis from the Research Materials Collection, administered under the direction of DOE. The program is responsible for the production, distribution, quality control, and reprocessing of the material in the Research Materials Collection. Applications for the loan of samples from this collection for nondestructive research projects germane to DOE programmatic interests are received at any time.

PERSON TO CONTACT FOR INFORMATION

J. G. Tracy
Stable Isotope Enrichment
Operations Division
Oak Ridge National Laboratory
P.O. Box Y
Oak Ridge, TN 37831

Phone:
Comm. (615) 574-0425
or FTS 624-0425

EN-TANDEM

Physics Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

The EN-Tandem is operated primarily as an atomic physics facility. The highest terminal voltage is 6.0 MV. The widest possible variety of ion species are available from a selection of ion sources. Two 90° magnets with a stripper (gas or foil) between them follow the accelerator so that a range of charge states is available for any ion at a given energy. Available facilities include (1) a merged electron–heavy ion beam apparatus with a merged region ~1 meter in length; (2) an ~14-meter flight tube with the capability of doing very small angle scattering and detecting individual charge states; (3) a Penning ion trap apparatus; (4) an Elbeck magnetic spectrograph with position sensitive detectors; (5) Si(Li) detectors and a curved crystal spectrometer; (6) data acquisition and analysis is performed using a CAMAC based VAX-11/750 computer system.

COLLABORATIVE USE

Collaborative experiments may be arranged with appropriate staff scientists or by a research proposal to the EN-Tandem manager.

PERSON TO CONTACT FOR INFORMATION

P. D. Miller Bldg. 5500 Oak Ridge National Laboratory P.O. Box X Oak Ridge, TN 37831	Phone: Comm. (615) 574-4781 or FTS 624-4781

TECHNICAL DATA

Beams	Most elements
Terminal voltages	0.3 to 6.0 MV
Source beam currents	Several hundred nA to several μA
Output currents	Up to 2 μA, depending on the ion species and charge state
Repetition rate	DC only
Magnet limitations	$ME/q^2 \leq 80$

HIGH FLUX ISOTOPE REACTOR

Operations Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

The prime purpose of the High Flux Isotope Reactor (HFIR) is to make research quantities of transuranium isotopes. Californium-252 is also produced as a by-product but is made available for the fabrication of neutron sources. These materials are produced in the flux trap in the center of the HFIR fuel element where a thermal-neutron flux of 3×10^{15} neutrons/(cm^2 · sec) is available to irradiate the curium target material. The HFIR is a beryllium-reflected light-water-cooled and -moderated, flux-trap reactor with a design power level of 100 MW. It burns 93% enriched ^{235}U fuel in aluminum-clad plates. Additional irradiation facilities are provided in the beryllium reflector around the fuel element to increase the production rate of the heavy isotopes.

The HFIR also has, as a secondary purpose, the performance of diverse irradiations, tests, and experiments which benefit from the exceptionally high neutron flux available. In the fuel element flux trap, a hydraulic-rabbit tube provides access to the maximum thermal-neutron flux in the reactor for short-term irradiations, and other positions are ideal for fast-neutron irradiation-damage studies. The beryllium reflector contains numerous experiment facilities with thermal-neutron fluxes up to 1×10^{15} neutrons/(cm^2 · sec). These facilities can accommodate static experimental capsules, complex fuel-testing engineering loops, and special experimental isotope irradiations, the targets for which are prepared by the Oak Ridge National Laboratory Isotopes Group. Four beam tubes are used for neutron-diffraction experiments and a small-angle neutron scattering facility sponsored by the National Science Foundation is available for use by researchers from universities, industry, and other national laboratories.

PERSON TO CONTACT FOR INFORMATION

B. L. Corbett Operations Division Oak Ridge National Laboratory P.O. Box X Oak Ridge, TN 37831	Phone: Comm. (615) 574-7001 or FTS 624-7001

TRANSURANIUM PROCESSING PLANT

Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

The objective of this program is to supply transplutonium elements for use in research. This involves operation of the Transuranium Processing Plant (TPP), which is the production, storage, and distribution center for the DOE heavy-element research program. Target rods are fabricated at TPP, irradiated in the High Flux Isotope Reactor (HFIR), and processed at TPP for separation, recovery, and purification of the heavy actinides up through ^{257}Fm. Since their construction in the mid-1960's, TPP and HFIR have provided the western world's supply of elements beyond curium (atomic number 96), either directly or by furnishing starting materials for further nuclear-synthesis reactions. The transuranium element isotopes produced in the TPP are used nationally and internationally to study the basic physics and chemistry of the transuranium elements. They are also being used in research and development programs relating to environmental effects, biological effects, and waste isolation.

PERSON TO CONTACT FOR INFORMATION

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Oak Ridge National Laboratory
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or FTS 624-7071

COMBUSTION RESEARCH FACILITY

Combustion Sciences Directorate
Sandia National Laboratories, Livermore
Livermore, CA 94550

Current activities at the Combustion Research Facility (CRF) supported by the Division of Chemical Sciences emphasize the development and the applications of new diagnostic techniques to the study of basic flames processes, as well as research in fundamental chemistry in combustion. (These programs are individually described elsewhere in this publication). In addition, DOE/Conservation sponsors programs at the CRF in combustion technologies, DOE/Fossil supports programs in coal combustion and related diagnostics development, and DOE/BES Materials Sciences supports programs in combustion-related materials research.

Complete facilities for resident and visiting researchers are available: offices for 60 staff, a meeting room accommodating 250 people, a laboratory building housing 14 independent experiments, special facility laser systems, a dedicated VAX computer, and access to a Cray computer.

The facility is located in Livermore, California, in the San Francisco Bay area, near major universities and other U. S. Government supported laboratories.

USER MODE

Qualified scientists are encouraged to take advantage of the specialized resources available at CRF. Prospective participants should submit a brief proposal to the laboratory director. Criteria for selection include technical merit, the extent to which CRF facilities are used, overlap with DOE program objectives, and the availability of specific equipment.

In general, the CRF will host visiting scientists to use the special-purpose lasers, work with resident staff, make use of computers and codes, and set up experiments. Visitors pay for their own salary, travel, housing, meals, and other local expenses. Facility lasers, apparatus, technicians, instrumentation, computers, and support-group services are provided without charge for research that is not proprietary. Research results from nonproprietary projects are expected to be published and disseminated.

For scientists with active government contracts, support for CRF research often can be arranged on an informal basis with the contract manager. There are opportunities for faculty, postdoctoral scientists, and graduate students to obtain Sandia support for combustion-related research at CRF.

In specific instances, proprietary research can be carried out at CRF. For this type of work, the DOE will be reimbursed on a full cost recovery basis for the use of all CRF resources. Details of a DOE Class Waiver for patent rights are available.

PERSON TO CONTACT FOR INFORMATION

Peter L. Mattern, Director
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Livermore, CA 94550

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or

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TECHNICAL DATA

Equipment	Key features
Flashlamp-pumped, tunable dye laser	Long pulse, high energy, high average power: 2-μsec 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 torr to 1 atm Mass spectrometer sampling probe LIF detection of radicals
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- or cylindrical-geometry burner 2-D axisymmetric laminar diffusion flame
Vertical turbulent diffusion flame	Open-circuit, induced-draft wind tunnel with co-flowing axisymmetric fuel jet: 30- by 180-cm viewing section to 6000 scfm flow
Combustion bomb	Simulated constant-volume engine combustion
Internal combustion research engines	Highly repeatable environment for homogeneous charge and diesel combustion studies
Experimental diagnostics research facilities	Laser fluorescence laboratory
Visitor laboratory	Rayleigh, Mie, and Raman 2-D imaging

STANFORD SYNCHROTRON RADIATION LABORATORY

Stanford Synchrotron Radiation Laboratory
Bin 69, P.O. Box 4349
Stanford, CA 94305

SSRL is a national facility for the utilization of synchrotron radiation in materials sciences, chemistry, biology, physics, medical science, and other disciplines. In addition to scientific research utilizing synchrotron radiation, the laboratory program includes the development of advanced sources of synchrotron radiation (e.g., insertion devices for the enhancement of synchrotron radiation, new ring designs) and the development of state of the art instrumentation for the utilization of synchrotron radiation.

The radiation comes from both the 4 GeV storage ring, SPEAR, and the 16 GeV storage ring, PEP. SPEAR is dedicated to the production of synchrotron radiation half of its operating time. Operation on PEP is parasitic with the high energy physics program. Presently SSRL has 22 experimental stations on 9 beam lines covering the spectrum from 5 to 45,000 eV. A second PEP beam will be in operation in November 1987. Specialized facilities for protein crystallography and lithography/microscopy are available. The beam line on PEP is an undulator beam line which provides the world's most brilliant photon beam at X-ray wavelengths.

USER MODE

SSRL is currently used by approximately 500 scientists from 101 institutions in 32 states and 10 foreign countries. Access to the facility is through a refereed proposal system. Proposals are due September 1 and March 1 each year. The booklet "General Information and Proposal Guidelines" available from SSRL contains information pertinent to proposal submittal. To date 1061 proposals for research have been received. Demand for experimental time is approximately twice that which can be accommodated.

PERSON TO CONTACT FOR INFORMATION

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TECHNICAL DATA

CHARACTERISTICS OF SSRL EXPERIMENTAL STATIONS

SSRL presently has 22 experimental stations, 21 of which are located on SPEAR and one on PEP. Nine of these stations are based on insertion devices while the remainder use bending magnet radiation.

	Horizontal angular acceptance (Mrad)	Mirror cutoff (KeV)	Monochromator	Energy range (eV)	Resolution, Δ/E	Approximate spot size, hgt × wdth	Dedicated instrumentation (mm)
			Insertion Device Stations				
Wiggler Lines–X-ray							
End stations							
IV-2 (8 pole)							
Focused	4.6	10.2	Double crystal	2,800 to 10,200	$\sim 5 \times 10^{-4}$	2 × 6.0	
Unfocused	1.0	–	Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 × 20.0	
VI-2 (54 pole)							
Focused	2.3	22	Double crystal	2,800 to 21,000	$\sim 5 \times 10^{-4}$	2.0 × 6.0	
Unfocused	1.0	–	Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 × 20.0	
VII-2 (8 pole)							Six-circle diffractometer
Focused	4.6	10.2	Double crystal	2,800 to 10,200	$\sim 5 \times 10^{-4}$	2 × 6.0	
Side stations							
IV-1	1.0	–	Double crystal	2,800 to 45,000	$\sim 5 \times 10^{-4}$	2.0 × 20.0	
IV-3	1.0	–	Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 × 20.0	Two-circle diffractometer
VII-1	1.0	–	Curved crystal	6,000 to 13,000	$\sim 8 \times 10^{-4}$	0.6 × 3.0	Rotation camera
VII-3	1.0	–	Double crystal	2,800 to 45,000	$\sim 10^{-4}$	2.0 × 20.0	
Undulator lines–VUV/soft X-ray							
V-2	1.5	–	Rowland circle multiple grating	10 to 1,200	≥7%	6.0 × 8.0	Angle integrated e^- spectrometer
Undulator lines–X-ray							
PEP 5B	Full	15.0	Double crystal	12,000 to 20,000	$\sim 10^{-4}$	0.6 × 6.0	
			Bending Magnet Lines				
X-ray							
I-4	2.0		Curved crystal	6,700 to 10,800	$\sim 0.3 \times 10^{-3}$	0.25 × 0.5	
I-5	1.0	–	Double crystal	2,800 to 30,000	$\sim 10^{-4}$	3.0 × 20.0	Area detector/CAD-4
II-2 (focused)	4.8	8.9	Double crystal	2,800 to 8,900	$\sim 5 \times 10^{-4}$	1.0 × 4.0	
II-3	1.0	–	Double crystal	2,800 to 30,000	$\sim 5 \times 10^{-4}$	3.0 × 20.0	
II-4	1.0	–	None	3,200 to 30,000		3.5 × 18.0	
Lifetimes port	1.8	–	None	1 to 6	Bandpass >10Å	4.0 × 0.4	
VUV/soft X-ray							
I-1	2.0		Grasshopper	32 to 1,000	Δλ = 0.1 to 0.2Å	1.0 × 1.0	
I-2	4.0		6m TGM	8 to 180	Δλ = 0.06 to 3Å	TBD	
III-1	2.0		Grasshopper	25 to 1,200	Δλ = 0.05 to 2Å	1.0 × 1.0	
III-2	4.0		Seyaka-Namioka	5 to 50	Δλ = 0.2 to 6Å	TBD	
III-3	8 to 10	4.5	UHV double crystal (Jumbo)	800 to 4,500	0.35 to 7 eV	2.0 × 4.0	
III-4	0.6		Multilayer	0 to 3,000	White or Δλ/λ=0.3%	2.0 × 8.0	Vacuum diffractometer/ lithography exposure station
VIII-1	12		6m TGM	8 to 180	Δk = 0.6 to 3Å	TBD	Angle resolved e^- spectrometer

FY 1987 EQUIPMENT FUNDS

Outlay funds of the Office of Basic Energy Sciences are divided among operating, equipment, and construction funds. Equipment funds are provided primarily to DOE laboratories. (Operating funds provided to other contractors are used for all costs, including purchase of necessary equipment.) FY 1987 equipment funds for Chemical Sciences programs were assigned as follows:

Facility	Equipment funds
Ames Laboratory	$ 590,000
Argonne National Laboratory	4,050,000
Brookhaven National Laboratory	1,456,000
Idaho National Engineering Laboratory	14,000
Lawrence Berkeley Laboratory	825,000
Los Alamos National Laboratory	40,000
Monsanto Research Corporation–Mound	20,000
Notre Dame Radiation Laboratory	280,000
Oak Ridge National Laboratory	1,150,000
Pacific Northwest Laboratory	235,000
Sandia National Laboratories, Albuquerque	50,000
Sandia National Laboratories, Livermore	577,000
Solar Energy Research Institute	110,000
Stanford Synchrotron Radiation Laboratory	725,000

INSTITUTION INDEX

SELECTED TOPICS OF GENERAL INTEREST

INVESTIGATOR INDEX