Molecular Science Research Center

1992 Annual Report

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and the Staff of the MSRC

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Opening Remarks

When we introduced the Molecular Science Research Center (MSRC) initiative in 1986, we wrote the following:

The sophistication and cost of instruments, equipment, and facilities used for molecular-level research are increasing steadily. As a result, it has become apparent that some of this work can best be done in a center similar to those that made possible the remarkable progress achieved in nuclear and particle physics over the past 50 years. . . . It is equally apparent that the MSRC will be most cost effective as a designated national user facility, available to scientists from universities, industry, and other national laboratories. The capabilities of the MSRC and its interdisciplinary culture can be expected to attract world-class molecular scientists in many fields who will bring their special expertise to bear on important national problems.

We envisioned a center where men and women from all areas of the scientific community—universities, government and industry research laboratories, and private R&D institutions—could come together to share and exchange ideas, concepts, experience, and expertise. That vision has taken on form and substance and become reality.

In 1992, the MSRC's Theory, Modeling, and Simulation group became a primary partner in the team selected to undertake a computational "Grand Challenge" for the U.S. Department of Energy's (DOE) Office of Scientific Computing. Our proposal for this project, *High-Performance Computational Chemistry: Scalable Algorithms for Grand Challenges*, was one of only six chosen for funding. The MSRC will conduct the research in partnership with Argonne National Laboratory (ANL) and five U.S. corporations. Three challenges have been targeted: safe thermal destruction of halohydrocarbons, binding of contaminants to clay minerals, and redesign of enzymes for enhanced biodegradation of contaminants in soil. Each area is critical to DOE's environmental mission, and each may have significant impact on environmental cleanup and new product development by industry. Project funding is expected to be about \$2.5 million over five years.

The MSRC hosted the West Coast Theoretical conference, which brought 170 scientists to Pacific Northwest Laboratory (PNL) in May 1992 and set an all-time record for attendance. The opening session was dedicated to Dr. Bowen Liu of IBM's Almaden Research Laboratory. Dr. Liu was a cofounder of the conference and a pioneer in the development of modern molecular electronic structure theory. The conference included oral and poster sessions on solution-phase chemistry, quantum chemistry I and II, and solid-state chemistry. Students were encouraged to participate in the oral presentations and were strongly represented.

Dr. John LaFemina of our Materials and Interfaces program worked with Professor John Yates of the University of Pittsburgh to organize a topical conference on environmental interfaces for the National Symposium of the American Vacuum Society. The symposium brought together researchers from chemistry, physics, surface science, and geochemistry to discuss basic science approaches to environmental problems. Our staff also participated in the annual symposium of the Pacific Northwest Chapter of the American Vacuum Society held at the Washington State University, Tri-Cities branch campus in Richland, Washington (WSU-TC). Highlights included an invited talk on surface science at the solid-liquid interface by Fred Wagner of the General Motors Research Laboratory.

In cooperation with Oregon State University, Washington State University (WSU), and the universities of Idaho, Oregon, and Washington, the MSRC established a Northwest Regional Lectureship in Physical Chemistry. The Lectureship will be awarded periodically to a physical chemist with an outstanding international reputation. The first recipient, Professor Rudolph A. Marcus, is the Arthur Amos Noyes Professor of Chemistry at the California Institute of Technology. During his visit to the Laboratory to receive the award, Dr. Marcus presented the lecture "Theory and Experiment in Electron Transfer Processes" at WSU-TC. Later in 1992, Professor Marcus received the Nobel Prize for Chemistry.

Throughout his career, Dr. Marcus's research has produced seminal contributions to the field of physical chemistry. He is probably best known for two major theoretical advances. The Rice, Ramsperger, Kassel, and Marcus theory is the most widely used tool for interpreting unimolecular reaction rates. Similarly, the Marcus Theory is the basis for modern theories of electron transfer in solutions, at electrodes, and in biological systems.

In October 1992, we held the kickoff meeting of the External Users Committee for the Environmental and Molecular Sciences Laboratory (EMSL) at the Battelle Conference Center in Seattle. The committee is chaired by Professor Bob Watts of the University of Washington. Other members include

- Professor Robert Griffin, Massachusetts Institute of Technology
- Professor Douglass Klarup, University of Montana
- Professor Edward Lazowska, University of Washington
- Professor Barbara Garrison, Pennsylvania State University
- Dr. Jerry Ebner, Monsanto Corporation
- Dr. James Harsh, Washington State University
- Professor Steve Kevan, University of Oregon
- Dr. Mel Koch, Dow Chemical Company
- Dr. Peter Taylor, San Diego Supercomputer Center
- Professor John Simon, University of California - San Diego.

The kickoff meeting was attended by 12 PNL staff members, who described the Laboratory mission and explained how the EMSL will help fulfill that mission.

The Pacific Northwest Laboratory joined a consortium of Northwest universities to develop special research capabilities of the Advanced Photon Source, which is currently under construction at ANL. A meeting was held in June 1992 at the University of Washington to develop plans for increased interaction between PNL and the Northwest universities in not only the development of the facility at the APS but also collaborative projects in which university professors and PNL staff

will join forces to use the unique APS capabilities to solve environmental restoration and waste management problems.

Our involvement with the Concurrent Supercomputing Consortium (CSCC) also accelerated during 1992. The 13 Consortium members, which include universities, research laboratories, government agencies, and industry, contribute to the acquisition and operation of shared computer resources such as the current systems—the 569-node Intel Touchstone Delta System, a 64-node Intel iPSC/860 hypercube, a file server, and associated peripherals. In return, members are entitled to a portion of these resources equal to their share of the Consortium's expenses for a period of three years.

The CSCC Annual Report for FY 1991-1992 includes reports on eight PNL research projects:

- Parallel Molecular Dynamics Simulation of Shape-Selective Separation in Zeolite Molecular Sieves: Butane and Isobutane in Silicate; J. B. Nicholas, R. J. Harrison, R. J. Littlefield, A. C. Hess (MSRC), and L. E. Iton (ANL).
- Massively Parallel Neural Net Approaches to Protein Folding; R. T. Miller (WSU) and J. B. Nicholas (MSRC).
- Coupled-Cluster Methods for Parallel Computer Architectures: The Protomeric Tautomerism of 2-pyridone and 2-hydroxypyridine Revisited; A. P. Rendell (Science and Engineering Research Council, Daresbury Laboratory, England) and R. A. Kendall (MSRC).
- Performance Visualization and Modeling, R. J. Littlefield (MSRC) and G. S. Thomas (PNL/Applied Physics Center).
- TEMPEST on the Delta, G. I. Fann (MSRC), A. S. Koontz, and D. S. Trent (PNL/Applied Physics Center).
- Tools and Techniques for Developing Parallel Computational Chemistry Applications; R. J. Littlefield and G. I. Fann (MSRC).
- Parallel Full-Potential Linearized Augmented-Plane-Wave Calculations; M. S. Stave and R. A. Bair (MSRC).
- Benchmark Electronic Structure Calculations; R. J. Harrison (ANL) and E. A. Stahlberg (PNL).

The project conducted by Harrison and Stahlberg was submitted in competition for a \$35,000 Intel Grand Challenge Computing Award offered by Intel Corporation and was one of four nominations receiving honorable mention. In addition, staff from PNL were part of a team assembled to provide courses on parallel computing, how to use the Delta system, and how to optimize code for i860 processors. Team members prepared class notes, gave lectures and demonstrations, and conducted sessions that gave users hands-on experience.

In parallel with the progress we were making in our research programs, we were moving forward with the EMSL project. Some of the highlights in 1992 are listed below:

- The Energy Systems Acquisition Advisory Board met in February and decided to maintain the total EMSL project cost at \$217.8 million.
- DOE granted approval to proceed with preliminary laboratory design.
- The architect/engineer, Zimmer, Gunsul, Frasca Partnership (ZGF) of Portland, Oregon, began the Title I design work in early April.
- The project scope was modified and the facility footprint was shrunken to reduce cost; and the Title I Design Report was issued with a total project cost of \$217.8 million.
- DOE Headquarters Validator, Ms. Sondra Kevelier, recommended that the project be supported at the requested level of \$53.2 million.
- A joint EMSL working group was organized of representatives from DOE's Offices of Energy Research (OER) and Environmental Restoration and Waste Management (OEM) and the Richland Field Office (DOE-RL).
- A joint EMSL working group comprising representatives of DOE's OER and OEM and the DOE-RL conducted an EMSL review in November.
- DOE issued a "Finding of No Significant Impact" in response to the EMSL Environmental Assessment.
- No formal reconciliation was necessary following a review conducted by the Independent Cost Estimate team; and DOE Headquarters granted approval to proceed with detailed design.

Recruiting also has proceeded well. Dr. Jiri Janata, formerly a professor in the University of Utah's Department of Materials Science and Engineering, joined the MSRC staff as Associate Director of the Materials and Interfaces program. While at the University of Utah, Janata also served as Director of the HEDCO Microengineering Facility. He began full-time employment in MSRC in January and has been actively recruiting scientists and post-doctoral associates for his group. Dr. Janata was invited to submit an entry to the Science pour L'Art Award competition and was one of eight U.S. finalists in the innovative category. He received his award at a ceremony in New York in October 1992.

Professor Paul D. Ellis, Department of Chemistry, University of South Carolina, accepted the position of Associate Director for the Macromolecular Structure and Dynamics program.

Dr. Lai-Sheng Wang was named to a joint appointment as faculty member at WSU-TC and a research staff member at PNL. Dr. Wang has been a Post-doctoral Fellow with Professor R. E. Smalley at Rice University since receiving his Ph.D. in physical chemistry from the University of California-Berkeley in 1989. His research interests lie in photoelectron spectroscopy applied to metal cluster molecules, molecule-cluster interactions, and high-temperature species.

During 1992, we added 13 scientists to our MSRC research programs, three each in Chemical Structure and Dynamics; Theory, Modeling, and Simulation; Materials and Interfaces; and Computing and Information Sciences and one in Macromolecular Structure and Dynamics. Dr. Bruce Kay, formerly with Sandia National Laboratories, is one of the new scientists in the Chemical Structure and Dynamics group. He has established an international reputation in gas-surface scattering, chemical kinetics, and laser spectroscopy.

Three staff members from the Theory, Modeling, and Simulation group collaborated with scientists and students from other laboratories and universities. Dr. Rick Ornstein was invited to serve as a Visiting Professor of Biophysics at the Roswell Park Cancer Institute in Buffalo, New York, where he trained and advised graduate students and participating on thesis committees. Mr. Robert Harrison visited R. J. Allen and M. F. Guest at the SERC Daresbury Laboratory to discuss collaborations that

will focus on the design and development of new parallel programming tools for use in chemical physics application. Dr. John LaFemina hosted Dr. Ann Bowler from Montana State University in a three-week collaboration at the MSRC on time-dependent Monte Carlo models of heteroepitaxy.

Mr. D. E. Knutson joined the EMSL project team as Research and Computer Equipment manager in August 1992. He is responsible for the successful, timely, and cost-effective completion of all tasks identified in the EMSL work plans. Two senior administrative staff also joined the EMSL project team.

In addition, we hired technical specialists for the Materials and Interfaces program and the Computing and Information Sciences program and enlisted nine postdoctoral associates.

Dr. Steven D. Colson, Associate Director of the MSRC's Chemical Structure and Dynamics program was a member of the National Research Council's Committee on Critical Technologies. The Committee's report, *Critical Technologies: The Role of Chemistry and Chemical Engineering*, was published last year. Colson also is the task leader in a program to develop new instrumentation for field and hot cell analyses. Staff from PNL's Applied Physics and Materials and Chemical Sciences Centers are participating along with staff from Westinghouse Hanford Company.

In 1992, the MSRC Colloquium Series brought more than 100 nationally and internationally renowned scientists to PNL, and our staff were involved in 112 collaborative projects with scientists in industry, universities, and other national laboratories. MSRC staff wrote or contributed to 154 publications, delivered 211 presentations, and hosted 106 seminars in 1992.

I believe this overview of our activities, along with the more detailed reports this document contains, clearly indicate that the MSRC is beginning to fulfill our expectations by attracting world-class molecular scientists in many fields.

While our immediate focus is on cleaning up the environment—remediating the legacy of past failures and oversights—ultimately our work will have a much wider influence. Nations around the world must deal with decades of environmental abuse and neglect. The U.S. Environmental Protection Agency estimates that America alone will be spending between \$174 and \$180 billion dollars per year by the year 2000. In addition, the Netherlands expects to spend \$100 billion to clean up the Rhine River over the next 20 years; and the World Watch Institute estimates that Poland will need \$20 billion, Czechoslovakia \$24 billion, and Eastern Germany more than \$250 billion, to clean up their respective environments.

Even more far-reaching effects of work such as that being conducted in the MSRC will concern its application to the prevention of future environmental contamination. In a global economy marked by intense competition among the developed, developing, and undeveloped nations, demands for energy can only be expected to escalate. Unless we find ways to make energy production environmentally benign, we will have lost the battle for sustainable economic development.

With the earth and its people at stake, the MSRC's world-class staff continued and expanded their vital work in 1992. Planned progress is included in nearly every section of this report, indicating the enthusiasm and optimism with which the MSRC staff looks forward to helping solve the problems of the future.

Michael L. Knotek
Manager, Molecular Science Research Center

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Chemical Structure and Dynamics

Chemical Structure and Dynamics

The Chemical Structure and Dynamics program is developed around several initiatives that respond to the need for a fundamental molecular-level understanding of chemistry required to meet the DOE's environmental and waste management needs. These needs are very broad, ranging from understanding health effects to the cleanup of contaminated sites. The Chemical Structure and Dynamics program in combination with other programs within the MSRC and other PNL research centers constitutes the broad range of capabilities required to identify and address the key scientific and technology issues. Specific Chemical Structure and Dynamics program elements are designed to focus on the DOE initiatives in understanding health effects, the processing and containment of mixed (chemical and radioactive) wastes, the reclamation of contaminated soil and groundwater, and the development of advanced analytical and characterization methods. The impact of the work is also expected to extend into many other fields essential to U.S. technological and economic strength.

The response to a mandate of this magnitude will far exceed the combined capabilities at PNL. Rather, we hope to be key players in the national effort. To the extent possible, our facilities and equipment are being made available for collaborative research with scientists from other laboratories, industry, and universities. Hence, you will note several staff listed in the following project descriptions with their affiliations footnoted. Researchers or organizations interested in a collaboration with PNL staff can contact either the MSRC management or specific staff members.

A significant addition to our staff in 1992 was Dr. X. (Sunney) Xie, who is expanding our efforts in real-time spectroscopy and developing a scanning near-field optical microscope for specially resolved surface spectroscopies. Our research staff now includes 13 research scientists and about 30 students, postdoctoral fellows, technical specialists, and other staff.

The overall research philosophy of the Chemical Structure and Dynamics program is built around the established relationship between structure and function, which is the underpinning of molecular science. The intent is to describe chemical processes at the molecular level in terms of the initial and final

structures, including measurements of the controlling energetics, rates, mechanisms, and real-time evolution of these structures.

The structural studies provide immediate insight into the nature of the condensed phase and are key to the direct comparison with theory by providing well defined targets for testing theoretical assumptions. This approach is particularly important in dealing with the complex problems associated with describing the molecule/substrate interface. Without good structural data, it will be very difficult to evaluate the quality of the potential functions that are needed to describe the molecular dynamics. The structural program is built around a combination of laser-based optical methods as well as atomic force and scanning tunneling surface microscopies.

Real-time measurements of the motions and chemical reactions on model substrates will have two direct consequences. First, they will provide new insights that will help shape the description of these phenomena in terms of molecular processes. Second, they will provide the data necessary for evaluating molecular dynamics theories that are being developed to describe molecular processes in terms of the kinematics of atomic nuclei on potential energy surfaces.

Another program initiative relies on the synthesis and characterization of microscopic models of condensed-phase chemistry. Atomic and molecular clusters are a form of matter whose properties lie outside the realm of general chemical experimental science. Thus, their study not only provides a quantitative basis for comparison with theory, but is also the source of a microscopic understanding of condensed-phase structures and dynamics.

The combination of state-of-the-art lasers and atomic resolution surface-mapping tools with traditional surface kinetics and characterization methods will be used to study interfacial chemistry and dynamics on extended structures. With this combination of tools, scientists can directly observe chemical processes on realistic chemical surfaces, and not be restricted to idealized single-crystal models. This initiative, in concert with the studies of molecular clusters, provides a new window through which we can observe new aspects of condensed-phase chemistry and

physics and, thus, expands our understanding of the chemistry of materials science in ways that are expected to have far-reaching effects.

The initiatives described above illustrate elements of a broad program that includes structure and dynamics studies of molecules in isolation, condensed in microstructures, in solution, and on extended surfaces. This multilevel, multidisciplinary approach allows us to study the component parts of complicated systems and to understand the complex chemical processes that occur in natural and man-made environments.

1. Single-Molecule Chemistry

L. A. Bumm, S. A. Joyce, and J. P. Cowin

Environmental problems such as soil contamination, and potential remediation techniques such as the catalytic destruction of chlorohydrocarbons, involve the adsorption of molecules on a surface. The scanning tunneling microscope (STM) is capable of imaging solid surfaces and molecular adsorbates with atomic-scale resolution. As a real-space probe, the STM can directly determine the role of surface structure, especially at defects such as steps, and vacancies in the adsorption and heterogeneous chemistry of molecules on surfaces.^(1,2)

A commercial, ultrahigh-vacuum STM and supporting surface analysis instrumentation was brought online in 1992. Atomic resolution images of graphite in vacuum can now be routinely obtained. The system capabilities have been enhanced with the addition of a load-lock system for rapid introduction of new samples and a thin-film evaporator for *in situ* deposition of clean metal and oxide surfaces. This STM will be used to look at adsorbates covalently bonded to surfaces.

Among the initial experiments planned are studies of photon and hot-electron-induced reactions of adsorbed chlorinated hydrocarbons. Previous results with macroscopic probes suggest that these reactions should be very sensitive to the adsorbate bonding geometry.⁽³⁾

At room temperature, many molecules of interest such as H₂O and simple hydrocarbons do not chemisorb, or they diffuse too rapidly to be imaged with an STM. Using a cryogenic STM operating at 20 K, diffusional motion can be frozen and the adsorption geometry of weakly bound molecules can be observed. During 1992, several laboratories with cryogenic,

ultrahigh-vacuum STMs were visited to determine the design principles. The design of PNL's low-temperature microscope was initiated in 1992. Construction and assembly of the microscope is planned for 1993.

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2. Structure and Dynamics of Size-Selected Cluster Ions

K. W. Brown and D. Ray

The synthesis of clusters in molecular beams affords the opportunity to create model systems that exhibit a rich variety of chemical phenomena. The application of techniques of optical spectroscopy to size-selected cluster beams facilitates rigorous studies of fundamental molecular processes in these model systems. We are currently initiating projects to study solvation, reactions, and adsorption in size-selected clusters with up to 100 constituents. This range of cluster sizes corresponds to a molecule or reactive system in solution surrounded by up to two solvation shells, an important size range for many-body effects on molecular processes.

The instrument that we have designed and constructed enables a wide variety of action spectroscopies to be performed on mass-selected cluster ions. For example, vibrational and electronic spectra can be obtained via photoabsorption spectroscopy, allowing determination of cluster size effects on the electronic structure of an ionic chromophore. Photoelectron spectroscopy of inorganic oxide cluster anions is also possible, yielding thermochemical and structural data on these important model species.

The cluster ion beam apparatus is shown schematically in Figure 2.1. Cluster ions are produced by crossing a pulsed supersonic expansion with a continuous,

Figure 2.1. Schematic of a cluster ion source and a tandem time-of-flight mass spectrometer with a time-of-flight photoelectron energy analyzer.

high-energy electron beam. The expansion drifts 15 cm prior to pulsed field extraction into the primary time-of-flight (TOF) mass analyzer. This analyzer incorporates a variant of the deHeer-Milani TOF scheme⁽¹⁾ and has 2-3 times the mass resolution ($m/\Delta m = 500$) as the traditional Wiley-McLaren TOF scheme in this application. Mass-selected cluster ions are intersected by laser pulses at the focus (SF1) of this primary TOF mass analyzer. Following laser interaction, a reflectron-type secondary TOF is employed to mass analyze the ionic photoproducts (SF2). Photoelectron spectra can be obtained by energy analyzing the photo-detached electrons by measuring their time-of-flight to a detector 1 m from SF1.

A current project is aimed at elucidating the structure of anion-water clusters. Recent theoretical work^(2,3) indicates that atomic anions occupy surface sites in anion-water clusters, not interior sites as do atomic cations in cation-water clusters. That is, atomic anions are not surrounded by water molecules in anion-water clusters for $n < 15$. This structure is seen most clearly in molecular dynamics simulations that show, on average, that a Cl⁻ anion resides 3-4 Å from the center of mass of the Cl⁻(H₂O)₁₅ cluster.⁽³⁾ This is in contrast to I₂⁻(CO₂)_n and Br₂⁻(CO₂)_n clusters, where the anion resides in the interior of the cluster.⁽⁴⁻⁷⁾ The structure of the anion-water clusters is determined by the competition between the water-water interactions and the anion-water interactions, and is sensitive to subtle differences in the potential energy surfaces.

Photoelectron spectra of I⁻(H₂O)_n clusters ($n < 60$) have been obtained by Cheshnovsky and coworkers^(8,9)

and have been interpreted as indicative of an interior anion for small clusters ($n < 16$) with the possible appearance of a surface anion state for larger clusters ($n > 30$). A mass spectrum of Br₂⁻(H₂O)_n clusters synthesized in our instrument is shown in Figure 2.2; Br⁻(H₂O)_n and (H₂O)_n⁻ clusters are also apparent in the mass spectrum. Analysis of the charged fragments following photoabsorption by these clusters will provide experimental data on the structure of these diatomic anion-water clusters. The measurement of observables that are related to cluster structure will provide comparisons between different theoretical models of ion-water and water-water interactions.

Figure 2.2. Mass spectrum of Br₂⁻(H₂O)_n clusters, with contributions from Br⁻(H₂O)_n and (H₂O)_n⁻ clusters also.

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3. Characterization of Photoinduced Charge Transfer Dynamics by Resonance Raman Spectroscopy

D. M. Friedrich, M. O. Trulson,^(a)
and J. P. LaFemina

Para-substitution on benzene with an electron-donor group and an electron-acceptor group results in an intense optical transition to a highly polar excited state. In the ground-state equilibrium geometry of cyanoaniline derivatives, this "charge-transfer" (CT) electronic state (1L_a) lies above the lowest excited singlet state (1L_b), which has "locally excited" (LE) character and lower dipole-moment. In some *para*-substituted aniline derivatives, dielectric polarization of the surrounding polar medium further drives charge separation by stabilizing the more polar 1L_a CT state below the 1L_b LE state. This solvent-relaxation and increased charge separation is thought to be accompanied by a large-amplitude twist about the ring-amine bond, leading to a twisted intramolecular charge transfer (TICT) electronic excited state. Formation of the TICT state in polar solvents quenches the shorter-wavelength fluorescence from the 1L_b LE state and reduces its lifetime ($\ll 1$ nanosecond). The TICT state is traditionally identified primarily by the properties of its fluorescence: a large Stokes shift, long-axis (1L_a) polarization, and longer lifetime (> 1 nanosecond).⁽¹⁾

Although some structural information about the CT state has been inferred from the effects of chemical substitution and solvent polarity on the emission dynamics of the LE and CT states, there is little detailed structural knowledge about the formation of the CT state due to the lack of structure in the broad absorption and CT-emission bands. Ultraviolet (UV)

resonance Raman scattering (static and time-resolved) from these excited states can provide more structural detail, especially when informed by bonding changes predicted by electronic structure calculations.

Static UV resonance Raman scattering intensities from *para*- and *meta*-N,N-dimethylaminobenzonitrile (DMABN) and *para*- and *meta*-aminobenzonitrile (ABN) reveal the electronic excited-state structural changes in the Franck-Condon region. Raman spectra of aminobenzonitrile compounds in polar and nonpolar solvents were recorded using excitation in the 1L_b (LE) and 1L_a (CT) absorption bands. Spectra excited at 266 nm (1L_a [CT]) in methanol are shown in Figure 3.1.

The observed enhanced modes are totally symmetric (depolarization ≈ 0.3), indicating simple A-term (non-vibronic) scattering. Resonance enhancements of Raman scattering intensities indicate the pattern of *initial* geometric changes on the 1L_a (CT) upper electronic surface following excitation. Electronic structure calculations (CNDO/S3) enable interpretation of these intensity enhancements (Figure 3.2).

For example, enhancement of scattering by the ring-breathing, deformation and elongation, and the CH-rocking modes indicates overall expansion and increased bond-alternation of the benzene ring. This is consistent with changes in the occupied molecular orbitals for this transition. Enhancement of scattering by the nitrile stretch in the *para*-substituted compounds is predicted by the increased antibonding charge density on the nitrile in the excited state, providing support for the traditional interpretation that the 1L_a state carries significant CT character. It is remarkable that in the *meta*-substituted compounds the nitrile stretch intensity is weak (*m*-ABN) or completely missing (*m*-DMABN) from the Raman spectrum resonant with the upper 1L_a state. The molecular orbital patterns again provide the reason: in *meta*-substitution, the nitrile lies nearly on nodal planes in both the upper and lower orbitals of the transition and, therefore, is uncoupled from the electronic transition. The excitation leads to little or no electron density changes on the *meta*-substituted nitrile.

This is the beginning of a more detailed understanding of the CT state and of the differences in the electronic couplings between the amine donor and the nitrile acceptor groups in these different compounds. Current theoretical models⁽²⁾ of the role of dielectric relaxation and solvent friction in driving the excited

(a) NORCUS postdoctoral appointee.

Figure 3.1. Resonance Raman spectra of cyanoanilines in methanol solution excited at 266 nm.

Figure 3.2. Molecular orbitals corresponding to locally excited and charge transfer transitions in *para* and *meta*-N,N-dimethylaminobenzonitrile.

state evolution from the LE surface to the stabilized CT surface require knowledge of the time development of the excited-state dipole during the solvent polarization process. In future experiments, resonance Raman spectral intensities in different solvents will test the limits of validity of continuum dielectric theories to describe the dynamics. A better understanding of the evolution of the structure of the TICT state will be developed through a comparison of time-resolved excitation studies of the evolving TICT state with electronic structure calculations and molecular dynamics simulations.

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4. Solution Phase Molecular Structure and Dynamics by Nonlinear Femtosecond Infrared Spectroscopy

G. R. Holtom and S. X. Xie

Understanding the influence of a solvent on chemical reactions requires a knowledge of liquid structure and dynamics. The structure of a molecular liquid is a dynamic one, undergoing constant fluctuations. For example, in liquid water, hydrogen bonds dissociate and reform on a picosecond time scale. The infrared absorption band in the O-H stretching region is very broad, mainly due to different types of hydrogen bonding. Spectral "hole burning" experiments in this spectral region can be used to study the inhomogeneity and the distribution of hydrogen bonding. However, on the nanosecond or longer time scale, the system should always be homogeneously broadened. In order to probe the "transient structures," femtosecond infrared pulses are needed. Questions concerning structure and fluctuation of fluids at the subpicosecond scale are important, for on a single-molecule basis chemical reactions occur at this time scale. Nonlinear femtosecond infrared spectroscopy is an attractive approach for studying the dynamic structures of liquids and their influence on the transition states of chemical reactions.

We are constructing an ultrafast laser system that can provide high-energy, high-repetition-rate, and stable femtosecond pulses. It involves the latest solid-state technologies, such as self mode-locking, Ti:sapphire regenerative amplification, and optical parametric oscillators. To date, most ultrafast infrared work has been limited to the 5- μm (carbonyl absorption) region. Our laser system will provide a tunable femtosecond infrared source, particularly around the 3- μm (hydrogen bonding) region, which will be used to conduct time-resolved vibrational spectroscopy in solutions. Nonlinear techniques such as photon echoes and time-dependent hole-burning will be explored to investigate the vibrational relaxation and dephasing times, and to elucidate the nature of interaction and fluctuation in liquids. These experiments will be particularly informative about the structure and dynamics of liquids containing hydrogen-bonding interactions.

5. A Tunable Diode Laser Infrared Spectrometer for the Study of Molecules and Weakly-Bonded Clusters in Low-Temperature Beams

T. A. Hu, E. L. Chappell, and S. W. Sharpe

Infrared spectroscopy is one of several powerful techniques that the physical chemist can call upon for studying the behavior of matter on an atomic scale. Two different but rapidly growing areas of science that have already benefitted from infrared techniques are weakly bonded clusters and atmospheric gases. Weakly bonded clusters of small molecules are promising systems for the study of chemical reactions on a microscopic level. They provide an opportunity to study energy transfer and vibrational relaxation processes in the regime between isolated molecules and the condensed state. Infrared spectroscopy has also been instrumental in studying atmospheric gases including H_2O , CO_2 , N_2O , CH_4 , and ClNO_3 , all of which are relevant to the study of greenhouse effects and ozone depletion.

High-resolution gas phase infrared spectroscopic techniques have traditionally been plagued by a number of problems including spectral congestion, Doppler broadening, and pressure broadening. Spectral congestion is related to the number of quantum states populated at a given temperature and is dictated by Maxwell-Boltzmann statistics. Doppler broadening is related to temperature through the

kinetic energy relationship but also involves the random three-dimensional (3-D) motion of the gas molecules. Pressure broadening is related to temperature through the collisional frequency of the molecules, which in turn depends on the density and velocity of the sample. By cooling and reducing the pressure of a gas sample, these three effects can be minimized, but at the expense of greatly reduced signal levels.

A relatively new technique, which takes advantage of the properties of rapidly expanding a gaseous sample into a moderate vacuum, has been used in our laboratory for the last year. A gas is expanded through a slit orifice that measures 5 in. long by 1/6000 in. wide. The resulting ribbon of gas expands at supersonic velocities, and in the process, molecules entrained in this gas are cooled to a few degrees above absolute zero. In addition, the random 3-D motion of the gas molecules is changed to a two-dimensional (2-D) flow with little velocity component in the plane of expansion but perpendicular to the mass flow. If infrared laser light is used to interrogate the gas molecules through the plane of expansion, spectral congestion, Doppler broadening, and pressure broadening are reduced significantly.

The interaction between sample and laser light is optimized by making multiple passes of the laser light through the ribbon of gas. This is accomplished by incorporating a custom-designed White cell optical arrangement into the vacuum chamber. Although the White cell increases our signal by about 30 times it also introduces a small (0.01% of total laser power) pseudo-systematic noise component that cannot be removed by simple subtraction techniques. A typical spectrum including this systematic noise appears in Figure 5.1a. This noise is common to almost all White cells, and is traced to scattered light. The sinusoidal pattern of the noise is due to étalon effects within the White cell. Recently, we have developed a scheme for avoiding this étaloning problem by mounting one of the White cell mirrors on a piezoelectric translation stage. In effect, the optical path length of the White cell is randomly changed during data acquisition and hence averages out the sinusoidal noise. Figure 5.1b contains a spectrum demonstrating the effects of dithering the White cell's length. This innovation has given us a tenfold increase in the signal-to-noise ratio.

We have recently obtained high-resolution infrared absorption spectra of the $\text{Ar-N}_2\text{O}$ dimer, whose intermolecular frequencies had been estimated from microwave data to fall near 40 cm^{-1} . Despite the weakness

Figure 5.1. Comparison of two spectra of the Ar-NH₃ dimer taken (a) without and (b) with noise correction. Identical spectral regions are covered in both spectra. The unique noise correction technique will now allow us to realize the full potential of the tunable diode laser infrared spectrometer.

of the studied band (approximately 200 times weaker than a typical vibrational fundamental), high-quality spectra were obtained with this equipment, and over 200 vibration-rotation transitions were observed and analyzed. Figure 5.2 shows experimental and simulated spectra of the Ar-N₂O dimer.

The observed band is a combination of the intermolecular bend with the highest-frequency intramolecular stretching fundamental of N₂O at 2224 cm⁻¹. Our analysis of this combination places its origin at 32.16 cm⁻¹ above that of the fundamental. The centrifugal distortion constants obtained in the analysis yield an independent estimate of 31.47 cm⁻¹ for the intramolecular bend. This agreement helps confirm that it is the intermolecular bend rather than the intermolecular stretch that is involved in the transition. The latter band, expected near 38 cm⁻¹ (from the centrifugal distortion analysis), does not appear in the spectra.

Figure 5.2. High resolution, rovibrational spectra of the nitrous oxide-argon dimer taken by tuning the diode laser over the region corresponding to the combination band involving an intramolecular stretch (ν_3 of N₂O) plus one quantum of intermolecular bending. Spectrum taken in under two minutes.

The combination state exhibits an anomalously large inertial defect of about 11 amuÅ²; that is, there is a discrepancy of this amount between the moment of inertia I_C and the moment sum $I_A + I_B$. The inertial defect must be equal for the average moments of a planar, strictly rigid rotor molecule, but not necessarily for the effective moments. This indicates a limitation in the degree to which the vibrational and rotational motions can be considered to be independent and is typical for a low-frequency in-plane bending motion of large amplitude. It thus confirms the participation of the intermolecular bend rather than the stretch in the observed combination transition.

Such results are of general interest in helping to understand the weak forces that bond such clusters and that are responsible for the initiation of condensation processes. They also are relevant to atmospheric modeling programs involving N₂O, which is a significant greenhouse gas.

6. Scanning Probe Microscopy Users Facility

M. J. Iedema

Since the invention of scanning probe microscopy (SPM) in 1981, users have found numerous new applications for it in such diverse fields as biochemistry and low-temperature physics. To further explore this capability, we have established a SPM Users Facility in the Chemical Structure and Dynamics program to make available the best commercial technology in scanning tunneling and atomic force microscopy, techniques that are suitable for the study of materials in air or in solution. To stimulate new research directions and to establish bridges with other research centers at PNL, we have encouraged scientists in PNL to explore the capabilities of this facility.

Some studies (many of which are ongoing) have included

- growth and dissolution of the mineral calcite (CaCO_3) in aqueous environments
- morphology of ultrapure optical thin films
- structure of catalytically active vanadium phosphate.

An example of recent research is the study of plasmid DNA that is chemically tethered to mica (Figure 6.1). The structure of these molecules can be studied, as

Figure 6.1. Image of plasmid DNA in an isopropanol solution. The image is approximately 440 nm across; the DNA molecule is about 3 nm high.

can the sites that are active for enzyme attachment and other chemical reactions.

7. Molecular Beam Surface Scattering and Kinetics

B. D. Kay

Molecular beam scattering from surfaces is a powerful experimental tool for studying the dynamics and kinetics of the interaction of molecules with surfaces. The coupling of surface science, molecular-beam, and laser technologies makes possible the measurement of total energy disposal and redistribution in gas-surface scattering. The major components of two molecular beam-surface scattering instruments have been transferred to the MSRC from Sandia National Laboratories. Previously, we have used these instruments to perform detailed surface kinetics and state-to-state scattering measurements of molecules interacting with metallic substrates. Renovation of the laboratory space for these instruments was completed in 1992. The instruments are in the process of being upgraded and reassembled, and are expected to be available for research experiments by mid-1993.

Initial experiments will focus on the dissociative chemisorption dynamics of halogenated hydrocarbons (e.g., CCl_4 , CHCl_3 , CH_2Cl_2 , CH_3Cl) on model oxide surfaces (e.g., MgO , SiO_2 , Al_2O_3). These studies will employ variable-energy supersonic molecular beams to determine energy-, angle-, and coverage-dependent dissociation probabilities. A variety of techniques, such as molecular beam epitaxy and/or chemical vapor deposition, will be explored to grow epitaxial thin oxide films on single-crystal metallic substrates. The successful synthesis of such crystalline thin oxide films will enable the entire arsenal of electron-based surface analytical techniques to be applied to the characterization of these nonconducting materials. In related experiments, the kinetics and dynamics of chemisorption and solvation of polar molecules on multilayer ice surfaces will be studied using molecular beams and temperature-programmed desorption. These experiments will help unravel the mechanism by which a strongly polar neutral molecule dissolves into an aqueous solvent and ultimately forms solvated ions. Sticking coefficients of prototypical electrolytes such as HCl and NH_3 on ice substrates will be determined as a function of translational energy and substrate temperature. The branching between molecular versus dissociative (solvation) chemisorption will

be probed using isotope exchange between the hydrogens of the electrolyte and the solvent substrate.

8. Solvation and Reaction Dynamics Studies via Spectroscopy and Dynamics of Molecular Clusters

R. Knochenmuss, D. Ray, and G. Holtom

This effort uses laser spectroscopic methods to study clusters of solvent molecules around or on prototype solutes. Since these clusters can be synthesized in sizes spanning the range from isolated molecules to bulk-like microcrystals or droplets, it is expected that their study will provide an explicit connection between microscopic and macroscopic properties. Of particular interest is the effect of solvation on chemical reactivity, both in the bulk limit and in small-scale environments relevant to interstices or to liquid-solid interfaces.

Solvents of great practical importance are those that hydrogen bond, particularly water. In such solvents, reactions involving generation or migration of charged species are among the most significant and also the most difficult to understand. This project addresses these issues through the study of excited state proton transfer reactions in hydrogen-bonded clusters (usually water). In these reactions, the "solute" molecule is selected for its increased acidity in its first electronic-excited state. This allows the reaction creating a solvated ion pair to be initiated with a laser pulse, which permits studying the course of the reaction using a variety of spectroscopic methods. These reactions are also expected to be unusually fruitful objects of study because the solvent is an active reaction partner and provides a stable environment.

The experimental apparatus has been largely assembled. This includes the dedicated cluster source, mass spectrometer, and dispersed or total fluorescence detectors. Shared equipment includes synchronized multiple nanosecond dye lasers, a picosecond dye laser, and a time-correlated-single-photon-counting system. The associated data collection and processing software are also completed.

Typical cluster distributions are shown in Figure 8.1, a mass spectrum of 1-naphthol*(H₂O)_n clusters with n up to about 60. The smallest of these clusters are unable to stabilize the proton transfer

reaction products⁽¹⁾ but are of interest because they have simple structures that provide insight into the nature of hydrogen bonds and are amenable to theoretical treatment. We have studied the ground-state vibrations of these clusters through nanosecond ion-dip spectroscopy, with particular attention to the intermolecular modes. The lack of a solvation-induced driving force for the reaction is evident in the remarkably low activity of these modes in the spectra, but enough is observable to make contact with recent high-level *ab initio* calculations on similar systems.⁽²⁾ Some vibrations of the naphthol moiety itself exhibit ion-dip depletions of greater than 50%, which is indicative of fast relaxation processes in the ground electronic state, possibly because of the presence of low-energy pseudo-bath modes of the solvent cluster.

The larger clusters in Figure 8.1 are known from fluorescence spectra⁽¹⁾ to undergo the proton transfer reaction. Initial experiments have been performed that address the dynamics of the reaction. The clusters were excited with 15-psec laser pulses, and the time dependence of the appearance of the product ion pair fluorescence was observed with time-correlated single-photon counting.

Figure 8.1 Mass spectrum of 1-naphthol*(H₂O)_n clusters, where n ranges from 0 to 60. The ions were created by sequential resonant 2-photon absorption of a ultraviolet laser pulse.

Results are shown for a range of cluster distributions in Figure 8.2. Each curve is made up of two components: one appearing in less than 60 psec, the other in 0.5 to 1.5 nsec. These are believed to represent the time scales for differing aspects of water solvent reorganization, and can be compared to the rate in room temperature bulk water of about 35 psec.⁽³⁾ The rate of product appearance decreases with increasing size (top-to-bottom). This is the correct trend because the reaction is quenched in ice.

That the reaction occurs at all is likely an indication that the clusters are in a "slushy" state; that is, they are neither rigid as in a crystal nor fully fluxional as in a liquid. This is a manifestation of the extremely small size of these systems, which result in a smearing of normally very sharp phase transitions over a

Figure 8.2. Fluorescence from large clusters, as selected by a filter that absorbs at wavelengths shorter than 400 nm. The traces are from distributions with up to 70, 100, 300, 400, 600, and 800 water molecules (top-to-bottom). Also shown is a sample two-component fit.

substantial temperature range,⁽⁴⁾ and allows access to molecular processes that are ordinarily too fast to observe.

Future research will focus largely on expanding the reaction dynamics data to obtain a broad picture of the solvent's role. This will include an improved fast fluorescence detection system and addition of a picosecond amplifier for use of pump-probe ionization-detected methods and possibly coherent wave mixing spectroscopies. In addition, the structures and bonding of the smaller clusters will be studied further using rotational coherence and/or high-resolution spectroscopy.

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9. Molecular Dynamics at the Water/Solid Interface

B. L. Maschhoff, M. Kwini, M. J. Iedema, S. A. Joyce, and J. P. Cowin

Reactions at the water/solid interface are crucial to understanding both soil and atmospheric environmental reactions. Efforts are aimed at two areas: interactions of ions at these interfaces, and charge transfer processes. In both studies, the water/solid interface is modeled using water multilayers adsorbed below 150 K (down to 50 K). At these temperatures, the vapor pressure of water is low enough to allow us to coat a normal sample (a 1-cm diameter disk) with arbitrary thicknesses of water. Other species are co-deposited into the water film to recreate solid/aqueous interfaces. Exploration of solvation and hydration processes, the electrochemical double layer, and ion-water-surface interactions are planned.

Several studies in 1992 examined water and other layers on a Cu(110) surface. One study examined the co-adsorption properties of a hydrophobic chlorinated

hydrocarbon molecule, CH_3Cl , and water. Figure 9.1 shows the thermal desorption of CH_3Cl after different initial coverages. Strong self-repulsion is evident in the first monolayer. If this experiment is repeated after first coating the surface with one monolayer of water, as shown in Figure 9.2, the binding energy of the CH_3Cl to the surface is greatly reduced for the first monolayer and the self-repulsion disappears. These and other studies show how water and chlorinated hydrocarbons compete for binding on the surface.

To study the structural aspects of these multilayers, an electron-stimulated desorption/ion angular distribution (ESDIAD) display was constructed that also allows very sensitive low-energy electron diffraction. Preliminary studies yield patterns for water adsorption that are indicative of the orientation of the O-H bonds at the surface. Work is beginning on thin-film deposition of oxides on a refractory single crystal substrate to provide convenient models of mineral-type surfaces.

These studies of ions at surfaces involve a collaboration between PNL and the University of Colorado where Professor Barney Ellison and his student

Figure 9.1. Thermal desorption of CH_3Cl from a Cu(110) surface for initial surface coverages of 0.2 to 2.0 monolayers (bottom-to-top).

Figure 9.2. Thermal desorption of CH_3Cl from a Cu(110) surface, as in Figure 9.1, after first coating the surface with a monolayer of water. The three curves are for 0.1, 0.3, and 2.0 monolayers of CH_3Cl .

John Biesecker are building an ion source to be delivered to PNL for shared use. The ion source will be capable of producing intense beams of positive or negative mass-selected molecular ions for deposition at very low energies.

10. Electron and Photon Stimulated Condensed-Phase Chemistry

T. M. Orlando and G. A. Kimmel^(a)

This program probes the chemical and physical effects of ionizing radiation, such as electrons and vacuum ultraviolet (VUV) photons on condensed atomic and molecular gases. Secondary electrons and cations are some of the principal products created during radiolysis of condensed-phase systems. These particles are often created with enough energy to initiate reactive scattering events such as anion- and

(a) Northwest Colleges and Universities Association for Science (NORCUS) postdoctoral appointee.

cation-molecule reactions, respectively. The study of ion-molecule reactions in the condensed phase and at interfaces is largely unexplored, particularly in the hyperthermal energy range. This is surprising, since these types of interactions are relevant to understanding important phenomena associated with condensed-phase radiolytic chemistry. Investigations include condensed-phase, ion-molecule reactions that are stimulated by electron- and/or photon-beam impact by probing both the ion and neutral reaction products.

The apparatus necessary for these experiments has been designed, and consists of a dispersed VUV laser light source and an ultrahigh vacuum system. The ultrahigh vacuum system is equipped with a quadrupole mass spectrometer, a TOF mass spectrometer, and a cryogenic sample holder for controlled multilayer "ice" formation. The TOF system is specifically designed to measure neutral yields and angular distributions using resonance-enhanced multiphoton ionization spectroscopy in conjunction with ion-imaging techniques.

The dispersed VUV source has been constructed and used to produce VUV radiation at 118.5 nm, 121.6 nm, and 143.2 nm using nonresonant third harmonic generation in rare gas mixtures.⁽¹⁾ This is done by focusing the output of a Nd:YAG pumped dye laser into a cell containing the tripling gas mixture. The VUV is separated from the fundamental UV by the chromatic aberration of the far-field LIF focusing lens⁽²⁾ and then detected with a vacuum Pt photodiode.

Studies of stimulated reactions in condensed amorphous and crystalline⁽³⁾ films of water are planned. We hope to determine the role of defect states and localization probabilities in stimulated condensed-phase reactions. An important extension of this work will be to probe the effects of coadsorbed species such as hydrocarbons on the dynamics of the stimulated reactions. We will also study electron and photostimulated processes on NaNO₃ substrates, since this salt is a main component of mixed (radioactive and chemical) wastes.

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11. Photodissociation of BrCH₂CH₂OH: Formation and Characterization of OH (X²Π)

S. P. Sapers and W. P. Hess

The reactions of free radicals with alkenes and alcohols play an important role in atmospheric chemistry, and in the chemistry of chemical/radioactive mixed waste storage and destruction. In particular, the reaction of hydroxyl radical with ethylene has been the recent focus of both experimental⁽¹⁾ and theoretical⁽²⁾ work. Electrophilic addition of hydroxyl radical (OH) to ethylene (C₂H₄) forms the hydroxyethyl radical, CH₂CH₂OH, which can react further, undergo the reverse dissociation reaction, isomerize, or decompose to other species, notably CH₂O and CH₃CHO. The particular fate of the CH₂CH₂OH radical depends on its internal energy content. The mechanism of CH₂CH₂OH decomposition is therefore germane to understanding the chemistry of the OH radical.

The product state distribution of OH (X²Π) following the secondary dissociation of excited hydroxyethyl radicals was measured:

The OH product states following initial photolysis was probed using LIF. The measured OH rotational and translational product distributions are in qualitative agreement with those predicted by modeling the dissociation dynamics of a highly rotationally excited CH₂CH₂OH radical, assuming the precursor is formed by an impulsive (primary) dissociation.

We produced excited CH₂CH₂OH radicals by 202-nm laser photolysis of BrCH₂CH₂OH in both unskimmed pulsed-jet and flow cell apparatus, and probed the unrelaxed OH state populations following CH₂CH₂OH dissociation using LIF on the OH (A²Σ⁺ ← X²Π) transition and collected the undispersed fluorescence. The pump-probe laser system uses two seeded Nd:YAG pumped dye lasers. The probe laser is the frequency-doubled output of a DCM/SR640 dye mixture, optimized for the wavelength range 306 to 314 nm, which is appropriate for exciting OH (A²Σ⁺ ← X²Π) transitions from v" = 0 and v" = 1. The linewidth of the

dye laser fundamental is 0.08 cm^{-1} . The **E** vector of the linearly polarized probe laser is oriented at ~ 54.7 degrees ("magic angle") with respect to the fluorescence collection axis to ensure that all transitions have equal probability of detection.

Figure 11.1 displays the LIF spectra of OH radicals produced following 202-nm dissociation of $\text{BrCH}_2\text{CH}_2\text{OH}$. Line assignments were made from published values.⁽³⁾ We extract the relative state populations by integrating the fitted peak areas and then dividing by the appropriate Einstein *B* coefficient. The relative OH state populations are displayed in Figure 11.2 along with Boltzmann plots of the F_1 and F_2 levels. The rotational distribution peaks at $N'' = 3$ or 4 for both spin-orbit states, and little population is found above $N'' = 9$. The Boltzmann plots display a maximum at $N'' = 3$ or 4 and, therefore, the distribution cannot be characterized by a "temperature." LIF spectra obtained in the jet using a room-temperature sample expanded with 800 Torr He are indistinguishable from the room-temperature flow-cell spectra within our signal-to-noise ratio. No spectral line assignable to transitions from $v'' = 1$ is observed.

The lineshapes of the observed OH transitions are well fit by a Gaussian function, but the linewidths are considerably broader than for room-temperature OH transitions. Any OH velocity vector parallel to the laser propagation direction shifts the absorption

Figure 11.1 Laser-induced fluorescence spectrum of the OH R branches following photodissociation of a 5-mTorr sample of $\text{BrCH}_2\text{CH}_2\text{OH}$ at 202 nm. The dye laser is scanned only over regions containing transitions.

Figure 11.2 (a) Relative OH rotational state distribution from 202-nm dissociation of $\text{BrCH}_2\text{CH}_2\text{OH}$. Open circles are A' levels of the $F_1(^2\Pi_{3/2})$ spin-orbit state. The triangles are the A' levels of the $F_2(^2\Pi_{1/2})$ state. One- σ error bars are ± 10 percent and are estimated from statistical analysis and our assessment of systematic error. (b) Boltzmann plot of the relative OH rotational state populations. The symbols are as in (a).

frequency and can serve to broaden the observed transition. The OH velocity can be extracted from the Doppler-broadened line profiles if the fragment velocity distribution is isotropic.⁽⁴⁾

The OH LIF linewidths for the flow-cell photolysis of $\text{BrCH}_2\text{CH}_2\text{OH}$ show no rotational-state dependence and have a FWHM of 0.6 cm^{-1} . The spectral linewidths measured in the jet expansion are also constant as a function of N'' , but are slightly broader than the cell values because of the spread in velocities of the unskimmed expansion. The most probable velocity from the FWHM linewidth, $\Delta\omega$, is extracted from the transition lineshape by deconvolving the 0.12-cm^{-1} laser linewidth and then assuming that the residual lineshape is the Doppler-broadened profile. The most

probable OH velocity is 2800 m/s, and corresponds to the sum of contributions from both the primary and the secondary dissociation.

The production of OH following the photodissociation of $\text{BrCH}_2\text{CH}_2\text{OH}$ occurs through a two-step dissociation mechanism. The rapid initial dissociation produces $\text{CH}_2\text{CH}_2\text{OH}^\dagger$ in a distribution of excited internal states, some of which have sufficient energy to undergo secondary dissociation to form OH and C_2H_4 . Although the partitioning of internal energy between vibrational and rotational degrees of freedom cannot be extracted from the TOF results, an impulsive dissociation model predicts that a large fraction of the available energy is partitioned into rotation.⁽⁵⁾

The simplest picture that describes how the rotating $\text{CH}_2\text{CH}_2\text{OH}$ fragment partitions its energy into the products applies the kinematics of a rigid rotator. The transition state (TS) structure of reaction⁽¹⁾ as well as the stable radical has been calculated by Sosa and Schlegel using *ab initio* techniques.⁽²⁾ The TS structure compared to the stable structure is planar along the HOCC frame with an increased C–O bond length (1.4 to 2.2 Å) and a decreased OCC angle (113 to 105°). We can estimate how the rotational energy of the $\text{CH}_2\text{CH}_2\text{OH}$ radical is partitioned into OH and C_2H_4 rotations and translations by assuming that an instantaneous C–O bond cleavage occurs while the radical is rotating *in the TS geometry*. The initial angular momentum of the system is derived from the initial impulsive dissociation using the ground-state $\text{BrCH}_2\text{CH}_2\text{OH}$ geometry. The model predicts that the bulk of the available energy (48 percent) is partitioned into OH translation while only 2 percent of the available energy is partitioned into OH rotation.

In summary, an average OH rotational energy is measured to be 8.2 ± 0.8 kJ/mole (Figure 11.2). The most probable OH velocity from the secondary dissociation is 2000 m/s, or 34 kJ/mole for the average translational energy. Conservation of linear momentum requires an average translational energy of 20 kJ/mole for C_2H_4 , so the total relative average translational energy release from the secondary dissociation is approximately 50 kJ/mole.

$\text{BrCH}_2\text{CH}_2\text{OH}$ is photodissociated in $\tilde{\text{A}}$ state, which results in a direct dissociation on a subpicosecond time scale. This primary dissociation produces $\text{CH}_2\text{CH}_2\text{OH}$ in a distribution of internal states, some of which have enough energy to undergo secondary dissociation, producing C_2H_4 and OH. The 202-nm

excitation of $\text{BrCH}_2\text{CH}_2\text{OH}$ results in a large degree of secondary dissociation. The impulsive model is used to describe the primary dissociation and implies that the $\text{CH}_2\text{CH}_2\text{OH}$ radical's excess energy is largely in rotation. Our OH product state results can be explained qualitatively by allowing some of the rotational energy to be channeled into C–O bond stretching, and, in combination with vibrational excitation, this ultimately leads to dissociation. The remaining energy is partitioned to the fragment rotation, translation, and perhaps C_2H_4 vibration.

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12. Kinetics of Methyl Radical Formation on Metal Oxide Catalysts

R. S. Smith, B. D. Kay, and S. D. Colson

Gas-surface interactions are important for determining reaction mechanisms involved in heterogeneous catalysis.^(1,2) Understanding these mechanisms may lead to advances in catalyst design for applications in the chemical industry and for the decomposition of hazardous chemical waste. In the past year, we have studied the catalytic oxidative coupling of methane, which leads to the formation of gas-phase methyl radicals and C_2 hydrocarbons.

Our approach involves the use of a microreactor that quenches the reaction through a supersonic expansion into vacuum. The expansion effectively quenches

gas-phase reactions because of attendant rapid cooling and greatly reduced collision rates. As a result, even very reactive species exist long enough to be ionized and, thus, detected using laser ionization mass spectrometry (LIMS). The primary advantage of this reactor is the capability for the direct detection of reactive intermediates and radicals. In addition, the apparatus is equipped with a quadrupole mass spectrometer for the detection of all other reactants and products (including H₂O, CO, and CO₂).

Previously we reported the relative yield of methyl radicals on a 1 percent Sr/La₂O₃ catalyst bed versus reactor temperature.⁽¹⁾ In this study, the yield of methyl radicals went through a maximum with increasing reactor temperature, peaking near 800°C. In subsequent experiments, the production of methyl radicals and ethene displayed different temperature dependencies. In an effort to more completely understand these observations, we have focused our research efforts on the kinetics of methyl radical formation.

To study the methyl radical formation reaction, the catalyst bed was modified to minimize both pressure gradients and residence times to avoid secondary reactions. Our results demonstrate that methyl radical production increases with temperature over the range 500° to 1000°C. An Arrhenius analysis of the data yields an apparent activation energy of about 20 kcal/mole. Furthermore, at all temperatures the methyl radical yield is nearly zero order in O₂ and first order in methane. These data are consistent with the reaction mechanism proposed by Gutman et al.⁽³⁾:

where S⁻ represents an active site on the surface. The active sites are regenerated by recombinative desorption of surface hydroxyls to form water. In related experiments, we have conclusively demonstrated that the previously observed maximum in methyl radical production⁽¹⁾ arises from depletion of OS⁻ sites along the reactor bed. This depletion is due to insufficient gas-phase O₂ to maintain the heterogeneous equilibrium depicted in Equation (12.1) above. We are presently examining the kinetics of the reactions responsible for the formation C₂ products such as C₂H₆ and C₂H₄.

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13. Dynamical Effects in Laser-Induced Particle Emission from Surfaces

G. Teeter,^(a) J. P. Cowin, S. Barlow, and T. Orlando

The interactions of laser photons with electrons in solids produce electronic and thermal excitations that result in intense photoemission of charged particles (electrons and ions) and neutrals. If a clean metal is irradiated with photons having energies greater than the substrate work function, intense photoemission of electrons occurs, producing high electric fields through the accompanying charge density outside the surface. This charge density, or "space charge," has been shown to have several important effects, which include the return of most of the electrons back to the surface as well as an interesting dynamical self-acceleration effect.⁽¹⁾ The dynamical acceleration effect was simulated by Gilton et al.⁽¹⁾ using an electron ballistic (EBAL) model that calculates the trajectories of the planes of charge emitted from the surface. Under realistic conditions, the space charge layer begins to sweep out as the laser beam turns off, resulting in a time-varying potential that can accelerate the electrons on the leading edge of the pulse.

The dynamical acceleration of photo-emitted H⁺ by the time-dependent space charge layer was explored using a modified version of the model used by Gilton et al.⁽¹⁾ and classical trajectory calculations. The EBAL code was used, modified to model the effects of

(a) Northwest Colleges and Universities Association for Science (NORCUS) Science and Engineering Research Semester Appointee.

a distribution of initial electron kinetic energies to determine the positions of the charge planes at steady state. These charge distributions were then used to determine the functional form of the potential as a function of current. Classical trajectories were then calculated using these potentials. It was found that H^+ can gain up to 1.75 eV because of dynamical acceleration, in addition to the 1.0 eV of available potential energy. This effect is greatest for ions that have barely escaped the image potential and are desorbing with low initial kinetic energies. Work is currently under way to investigate screening effects in the space-charge layer. These studies will be extended to wide band-gap materials since several studies report laser desorption of ions with unusually high kinetic energies from band-gap materials.^(2,3) Defect sites, band-gap states, and multiphoton transitions are expected to strongly affect the yields and energy distributions of the photoemitted particles.

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14. Near-field Optical Spectroscopy

S. X. Xie, E. V. Allen,^(a) and S. A. Joyce

In recent years, near-field optical microscopy^(1,4) has emerged as a new area of scanning probe microscopy. Near-field optical microscopy involves scanning a spot of light of a dimension much smaller than a wavelength across the surface of a sample. Recently, a technique developed by Betzig et al.⁽⁵⁾ for pulling an optical fiber has proved able to fabricate fiber tips with 15-nm diameters. When the distance between the ultrafine fiber tip and the sample is sufficiently

small (10 nm), the spatial resolution is limited only by the cross-section of the tip, and can be much higher than the far-field diffraction limit in ordinary optical microscopes.

While this technique has numerous potential applications, such as surface imaging and optical storage, we are exploiting the capability of conducting molecular spectroscopy at the nanometer scale. This would make possible implementing the wealth of techniques of optical spectroscopy with an unprecedented spatial resolution, providing information about molecular species and their chemical reactions not accessible with scanning electron microscopy, scanning tunneling microscopy, and atomic force microscopy. The high time resolution afforded by optical measurements would allow observations of real-time dynamics.

Construction of a near-field optical microscope is near completion. Our design provides the superb sensitivity required for critical measurements. Development of the instrument is aimed at conducting optical spectroscopy (steady-state and time-resolved) on a single-molecule basis (a single chromophore or a single macromolecule with many chromophores). Potential applications will be explored in several areas, such as developing a new surface analytical tool for characterizing nanostructures of multicomponent/multiphase systems. Other potential applications include spectroscopic mapping of the photosynthetic membrane, elucidating its local structure and biological functionality; and real-time imaging of DNA and chromosomes.

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Environmental Dynamics and Simulation

Environmental Dynamics and Simulation

The MSRC Environmental Dynamics and Simulation program combines expertise from PNL's Earth and Environmental Sciences Center with programs funded through DOE's Offices of Technology Development and Basic Energy Sciences to address fundamental problems in restoration of contaminated subsurface regions. Basic research in this program is performed to develop innovative remediation concepts through advances in the understanding of the reactions of contaminants in the geochemical environment. At the microscopic level, each reaction is controlled by molecular-scale phenomena, which, if fully understood, can form the basis for marked improvement in our ability to predict contaminant form and movement and to devise remedial cleanup measures for contaminated environments. Thus, the focus of the Environmental Dynamics and Simulation research program is to integrate macroscopic, microscopic, and molecular level understanding of the reactions between environmental contaminants and geological materials that occur at the solid:liquid interface and eventually the liquid:liquid interface.

The Environmental Dynamics Laboratory will be equipped to perform direct measurements of aqueous speciation of solutes, and of the bonding environment and speciation of sorbed solutes in colloidal suspensions. Research to evaluate mechanisms, thermodynamics, and rates of reactions at the surfaces of heterogeneous natural particles, such as clay minerals, oxides, carbonates, and organic material, will be a major focus of the facility. The laboratory will be linked to the Molecular Science Computing Facility (MSCF). This linkage will enable the modeling calculations of solution and surface equilibria, reaction kinetics, diffuse double-layer properties, molecular dynamics, and thermodynamic/molecular/electronic properties of organic molecules, inorganic ions, and solids that are needed to interpret and simulate research on the surface chemistry and reactivity of natural mineral and organic particles. These calculations will then serve to underpin large hydrogeochemical simulations of contaminant transport using the high-performance computing capabilities of the MSCF.

1. Synchrotron Development

J. E. Amonette, S. V. Mattigod,
K. J. Cantrell, and D. L. Blanchard

An important aspect of the Environmental Dynamics and Simulation program is the development of expertise in the application of synchrotron radiation to geochemical problems. Synchrotron sources offer very intense, highly collimated, tunable, and essentially monochromatic radiation in the x-ray, ultraviolet, and infrared spectral regions.

Research incorporating synchrotron techniques can be done on samples under conditions approaching those in the environment. Spectroscopic and diffraction studies can be performed with much higher resolution than by conventional methods and kinetic studies with half-lives on the order of micro- and nanoseconds are possible.

This year, staff members performed some preliminary x-ray absorption spectroscopy studies on Pb and Ni compounds at the National Synchrotron Light Source at Brookhaven National Laboratory. The focus of the work was to attempt to distinguish between the oxide, hydroxide, carbonate, and hydroxycarbonate forms of these elements.

As part of a larger study to assess the release and migration of lead from submarine reactor cores disposed at the Hanford Site,⁽¹⁾ thin wires of metallic lead were equilibrated with Hanford groundwater for several months. Aliquots of the equilibrium solutions were taken and analyzed for lead. The results of these analyses indicated possible equilibrium with either PbCO_3 (cerussite) or $\text{Pb}(\text{CO}_3)_2(\text{OH})_2$ (hydrocerussite). X-ray diffraction analysis of scrapings from the lead wires suggested hydrocerussite was present. An x-ray absorption spectrum of the scrapings (see Figure 1.1) was similar to that obtained for a hydrocerussite standard and easily distinguished from another oxidized lead compound, $\text{Pb}(\text{OH})_2$. Although a spectrum for PbCO_3 was not obtained, the x-ray absorption spectra were compatible with the x-ray diffraction results and suggest

Figure 1.1. X-ray absorption spectra across the Pb-L_{III} edge for two standard Pb compounds and for whitish precipitates that formed on the surface of Pb wire during equilibration with Hanford groundwater.

that this technique may prove quite useful in future studies of sparingly soluble compounds in soil and groundwater systems.

Staff members are continuing their participation in the Pacific Northwest Consortium beam-line proposal for the Advanced Photon Source at Argonne, Illinois, and have joined another consortium formed to build a beam-line for the study of actinides at the Advanced Light Source in Berkeley, California.

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Macromolecular Structure and Dynamics

Macromolecular Structure and Dynamics

The primary research goals of the Macromolecular Structure and Dynamics program are focused on the application of nuclear magnetic resonance (NMR) and mass spectrometry (MS) techniques to the analysis of complex interactions between environmental pollutants and components of the subsurface media, and the effects of these pollutants on the structure and dynamics of biological macromolecules. Leading-edge NMR and MS instruments with high resolution and sensitivity are being developed for measurements on the primary, secondary, and tertiary structures of large biomolecules. Other applications of these instruments include analysis of trace components in complex environmental mixtures, microimaging of physical and biological structures, measurements of solute flow profiles in heterogeneous materials such as soil, analysis of gas-phase and solution-phase chemical dynamics, studies on interfacial adsorption processes, and analysis of the structural integrity of solid-state materials such as vitrified wastes.

During the past year Dr. Paul D. Ellis was appointed as the Associate Director of the Macromolecular Structure and Dynamics program. He was formerly a Professor of Chemistry at the University of South Carolina.

Nuclear magnetic resonance spectroscopy has become a widely used technique for determining the 3-D conformation of biological macromolecules in solution, both in their native states and in perturbed states resulting from the interaction of environmental pollutants, drugs, and other substances. Included in the NMR program plan is the development of the first 1000-MHz (gigahertz) spectrometer, which will enable a complete structural analysis to be made of the solution-phase structures of large macromolecules. For example, the gigahertz NMR spectrometer is expected to provide new capabilities for investigating the structures of biodegradative enzymes, biosensor materials, and a variety of large proteins that are involved in the regulation of cell and tissue growth in normal and cancerous states. The structures of many of these molecules cannot be completely characterized using commercially available NMR spectrometers that operate at frequencies up to 600 MHz.

The magnetic resonance program is headed by Dr. Gary P. Drobny, who holds a joint appointment as a Professor of Chemistry at the University of Washington. He will lead the development of the gigahertz NMR spectrometer's radio frequency (RF) system and console, and will assist in the deployment of conventional instruments for both solution-phase and solid-state NMR research in the EMSL. During the coming year the magnetic resonance program will be extended to include research using the technique of pulsed electron paramagnetic resonance.

Progress has continued during the past year in the development of the first gigahertz NMR spectrometer, as described in Section 1 of this chapter by Dr. Thomas S. Tenforde, the Acting Manager of the MS&D program during the period 1988-1992. Also described in this year's report is progress on the design of the RF system and console for the gigahertz spectrometer, and applications of NMR in research on deoxyribonucleic acid (DNA) structure and the interfacial chemistry of materials adsorbed onto solid surfaces.

The MS component of the Macromolecular Structure and Dynamics program is developing an enhanced understanding of biological processes at the molecular level using new MS methods. Research efforts have been undertaken to understand reactions and interactions of biomolecules relevant to such diverse topics as environmental cleanup by bioremediation procedures, effects of chemical pollutants and radiation on human health, and identification and structural characterization of new biomarkers of chemical and/or radiation exposure. These research objectives are being augmented by the development and application of MS methods with high sensitivity and resolution. The advanced instrumentation being developed as part of the EMSL project includes an ultrahigh-resolution ion cyclotron resonance mass spectrometer, along with ancillary equipment necessary to support the overall MS research effort. The advanced capabilities provided by these major instruments are projected to provide the sensitivity necessary to study biochemical processes at the cellular level (e.g., in the quantitation of DNA adducts). As part of the effort to identify new biomarkers, the ultrahigh-resolution MS instrumentation will be

applied to studies of minor structural modifications in proteins and large DNA segments.

This year's annual report describes advances in several aspects of the MS program headed by Dr. Richard D. Smith. Sections 5 through 11 of this chapter describe research that has been directed primarily at the development of new instrumentation for probing the structure of large biopolymers. Also described is progress in developing the necessary ancillary methods for biopolymer structural characterization (e.g., on-line separation methods such as capillary electrophoresis).

1. Progress in the Development of a Gigahertz NMR Spectrometer

T. S. Tenforde

The first gigahertz NMR spectrometer is being developed to provide increased resolution and sensitivity for studies on solids, interfacial adsorbates, and solution-state structures of large macromolecules. The present generation of commercially available NMR instruments, which operate at frequencies up to 600 MHz, are capable of characterizing the 3-D structures of biomolecules with molecular weights approaching 20 kilodaltons. When used in combination with specific isotope labeling for heteronuclear measurements, a gigahertz spectrometer is expected to greatly extend the size range of proteins and nucleic acids for which solution structures can be characterized by NMR. In addition, the gigahertz NMR spectrometer will provide increased sensitivity and resolution for studies on solid-state materials and surface adsorbates.

Development of the gigahertz NMR spectrometer is organized into five subtasks:

1. Measurement of properties such as critical current density and voltage-current characteristics of several candidate superconducting materials for the 23.5-tesla magnet; fabrication and testing of prototype magnets from materials showing the greatest promise in short-sample tests; and selection of the optimum superconducting materials for the full-scale magnet system.
2. Design and fabrication of the full-scale 23.5-tesla spectrometer magnet.
3. Development of the RF system and operating console.

4. Selection and acquisition of the data analysis computer and workstations.

5. System integration and performance tests.

During the past year, contracts were awarded for Subtask 1 to Wang NMR, Inc., in Livermore, California, and to the Francis Bitter National Magnet Laboratory at the Massachusetts Institute of Technology (MIT) in Cambridge, Massachusetts. Eight niobium tin superconducting materials, doped with either titanium or tantalum to optimize the current density, are currently being subjected to extensive tests of mechanical, electrical, and magnetic properties at field levels up to 23.5 tesla using the Hybrid 2 magnet at MIT. In 1992, short-sample tests on one-meter lengths of wire were completed using four superconducting materials obtained from two manufacturers. These materials exhibited critical current densities ranging from 4000 to 8700 A/cm² when tested at an operating temperature of 1.8 K and a total field level of 23.5 tesla (the flux density corresponding to a proton Larmor frequency of 1000 MHz). A critical current density of 5000 A/cm² or higher was achieved by three of the superconducting materials when placed under mechanical tension to maximize the current density. Since 5000 A/cm² is estimated to be the minimum critical current density required to reach the target field level of 23.5 tesla in the full-scale NMR magnet, the results of these initial tests are encouraging. After conducting similar performance tests on the remaining four wires, the most promising superconductors will be wound into prototype solenoid coils containing more than one kilometer of wire for further tests at 23.5 tesla in the MIT Hybrid 3 magnet. Completion of these tests is scheduled for the summer of 1993.

A request for proposals (RFP) was issued in August 1992 for development of the full-scale 23.5-tesla magnet for the gigahertz NMR spectrometer. Several bids were received and the technical and cost evaluations have been undertaken. It is anticipated that a contractor for this work will be selected in 1993, and the design and development of the 23.5-tesla magnet will commence by late 1993. Work on the design of the RF system and console for the instrument was initiated by G. P. Drobný at the University of Washington in 1992, as described in the following section of this chapter.

2. Preliminary Console Design for a 1000-MHz NMR Spectrometer

G. P. Drobny^(a)

The development of a gigahertz NMR spectrometer involves the design of a new RF pulse system and console that differ significantly from those used with commercially available 500-MHz and 600-MHz spectrometers. In this section conceptual designs are described for both the RF System and console of the gigahertz NMR spectrometer.

Figure 2.1 presents a functional block diagram of the gigahertz spectrometer console. The host computer is interfaced directly to the data acquisition processor (DAP) and the pulse programmer. The DAP handles the real-time collection of data and passes the data on to the host computer when it is required to update a display or write the data onto disk. The pulse programmer generates all the timing signals that control the NMR experiment. Working together, the DAP and the pulse programmer perform an NMR experiment. The host computer is used only to provide the operator interface, load necessary commands into the pulse programmer and DAP, display data, write data to disk, and after the experiment is concluded, analyze the data. An important feature of this arrangement is the direct communication between the pulse programmer and the DAP, which allows the pulse programmer to control the manner in which the DAP collects and processes the data.

To perform an NMR experiment, the pulse programmer generates signals that instruct the RF transmitters to produce pulses of specified amplitude, duration, frequency, and phase. This RF power is applied to the NMR probe via the duplexer, to generate an RF field in the probe coil that irradiates the sample. The resulting NMR signal passes from the probe to the RF receiver (see Figure 2.1) and is ultimately detected in quadrature relative to the transmitter carrier frequency. The NMR free induction decay (FID) signal is filtered appropriately, and applied to analog-to-digital converters (ADCs) for digitization. The timing signals that strobe the ADCs originate from the pulse programmer and the resulting data pass to the DAP. The DAP performs all necessary signal averaging functions.

(a) The author holds a joint appointment in the MSRC and the University of Washington in Seattle, where he is a Professor of Chemistry.

Progress during 1992 was centered around development of novel pulse programmer designs for use in the gigahertz NMR spectrometer. Any pulse programmer design development must perform the widest possible range of current multidimensional and multipulse NMR spectroscopy and microimaging experiments, as well as be conveniently expandable to accommodate new experimental techniques. Recent generations of commercial pulse programmers have not been expandable, and thus most commercial instruments are not easily restructured to perform new pulse techniques without costly and time-consuming incremental upgrades.

Pulse programmer designs that are being considered fall into two general categories: loop-oriented state machines and more structure-free systems. State machine architecture has been successfully employed in the pulse programmers of several NMR spectrometers at the University of Washington. In this design the NMR experiment is described as a sequence of states, where each state describes the condition of all electrical outputs for a specified period. Pulse programmer state architectures differ in the organization of their state memory and the methods that they use to determine the sequence in which the states should be expressed. The design used at the University of Washington organized memory as a linear array of 4096 addressable words. Each word is 80 bits wide, the size of one state. State words are retrieved from memory sequentially unless specified otherwise by the loop field. The loop field specifies a loop count, the number of times an action should be repeated before the next state in the sequence is executed.

The principal disadvantage of the state machine design is that the loops are invariant. In other words, when a loop occurs, the sequence of states within the loop must be exactly the same for each iteration of the loop. This is a serious limitation because it is common to repeat NMR experiments where the states of subsequent iterations are perturbed in some way (e.g., pulse phase changes, amplitude changes, etc.). This limitation can be overcome in certain cases, but the solutions of this problem are not general.

As a result of the limitations inherent in state machine architecture, we have turned toward developing a pulse programmer with a more "structure-free" architecture. This means that the pulse programmer architecture should not impose restrictions on the possible sequence of states in the NMR experiment. A first step toward developing a "structure-free" pulse programmer was taken almost 20 years ago

Figure 2.1. Block diagram of 1000-MHz NMR spectrometer console.

with the introduction of first in/first out (FIFO)-driven pulse programmers. Unfortunately, such programmers, though very versatile in principle and easily expanded horizontally, lacked vertical depth due to limited FIFO memory size.

Also, the inherently slow speed of host computers available at the time required interposing a microprocessor between the host computer and the pulse programmer. The problem of limited FIFO memory no longer exists and the speed of modern workstations probably makes the microprocessor buffer unnecessary. We have therefore considered two FIFO-based pulse programmer designs, shown in Figure 2.2. The design shown in Figure 2.2a is typical of a "brute force" FIFO-based pulse programmer, which features a wide array of FIFO devices, input-serviced by a state assembly register with outputs directed toward an output register field (e.g., an RF switch control) and a timer control. A more compact

design shown in Figure 2.2b utilizes a "narrow" FIFO. Each memory input is composed of two parts: a 16-bit data field and an 8-bit "tag" field. The tag field specifies the section of the state assembly register for which the data field is destined. As the steering logic removes each item from the FIFO it examines the tag field and loads the data field into the assembly register. At this point the contents of the state assembly register are loaded into the output register and the timer.

The FIFO-driven design for pulse programmers is not only simple but also easily expanded to address the ever-increasing complexity of NMR experiments. The RF gates, DC gradient pulsers, etc., can be accommodated by the addition of more memory and a minor expansion of the steering logic. During the next year, a FIFO-driven pulse programmer design will be completed and a pulse programmer prototype will be produced and tested. DAP designs will also be completed, and a DAP will be prototyped.

Figure 2.2. Two alternate FIFO-based pulse programmer designs.

3. NMR Evidence for Sequence-Dependent DNA Mobility

M. A. Kennedy, B. R. Reid, and
G. P. Drobny^(a)

During the past year, our research has focused on studying the structure and dynamics of nucleic acid biopolymers. The following example illustrates how we have used solution-state ^1H NMR spectroscopy to discover sequence-dependent mobility in a family of related DNA oligonucleotides that contain a common

(a) M. A. Kennedy is a NORCUS postdoctoral fellow who holds an Alexander Hollaender fellowship awarded in 1991 by the U.S. Department of Energy. B. R. Reid and G. P. Drobny are professors of chemistry at the University of Washington in Seattle. Dr. Drobny also holds a joint appointment with the MSRC as head of the NMR program.

endonuclease restriction site, $\text{TT}\downarrow\text{AA}$. The mobility is found to occur at the TpA junction, which is the cleavage site for the phosphodiester backbone.

Since 1987 there have been several solution-state NMR and combined NMR/molecular dynamics studies⁽¹⁻⁷⁾ of the structure of synthetic DNA oligomers containing A_nT_n and T_nA_n segments. DNA sequences that contain adenine and thymine tracts are of interest because of their intrinsic bending properties. A general structural feature of A_nT_n tracts has emerged from these NMR studies; the minor groove width, which can be probed in solution by measuring the $(n)\text{A-H2}$ to $(m+1)\text{-deoxyribose-H1'}$ crosspeak in 2-D nuclear Overhauser enhancement (2D-NOESY) spectra, is progressively narrowed from the 5' to 3' end of an A-tract. The minor groove width compression along adenine runs is likely related to the mechanism for sequence dependence formation of UV-induced pyrimidine-dimer photoproducts.⁽⁸⁾ In a study by Brash and Haseltine,⁽⁸⁾ a fivefold variation in the frequency of formation of thymine dimers occurred in a TTTTC segment; the propensity for dimer formation is greatest at the 3' end of the thymine run (i.e., the 5' end of the complementary adenine run). Thus, it appears that thymine dimer formation is repressed as the minor groove width is narrowed. This effect may be related to a change in the pyrimidine base-stacking that is associated with the narrow minor groove structure. Minor groove width compression in adenine tracts has also been implicated in the retardation of hydroxyl radical cleavage of the phosphodiester bond in the backbone of duplex DNA.⁽⁹⁾

Mobility at the TpA Junction

In solution-state NMR investigations of DNA structure, given the sparsity of nonexchangeable protons in the interior of the DNA helix, the ability to probe the minor groove width relies almost exclusively on reliably quantifying the $(n)\text{A-H2}$ to $(m+1)\text{-H1'}$ crosspeak intensity. Here we report a general and unusual broadening of the proton resonances of the adenine base that occurs at the TpA junction in T_nA_n -containing DNA oligomers (when $n > 2$). Specifically, in 500-MHz ^1H NMR experiments, the H2 and H8 protons of adenine, which reside in the minor and major grooves of duplex DNA, respectively, are observed to be unusually broadened (see Figures 3.1 and 3.2) in the DNA oligonucleotides $[\text{d}(\text{CGAGGTTTAAACCTCG})_2]$, $[\text{d}(\text{GCTCCTTTAAAGGAGC})_2]$ and $[\text{d}(\text{GCCGTTAACGGC})_2]$. In 16-mers that contain

Figure 3.1. The 500-MHz ^1H spectrum of the aromatic region in $[\text{d}(\text{CGAGGTTTAAACCTCG})]_2$ measured at 31°C . The adenine H2 protons are labeled A3, A9, A10, and A11. The corresponding adenine H8 protons are clearly labeled.

C_2A_3 , G_2A_3 , and A_3T_3 tracts, all adenine proton resonances are narrow, indicating that the broadening occurs only at TpA steps in T_nA_n tracts. The usual mechanisms that lead to differential linewidths for aromatic protons in DNA (e.g., unresolved J coupling or strong fluctuating dipolar interactions) do not account for the increased linewidths. Other line-broadening mechanisms such as paramagnetic impurities, imino proton exchange, and hairpin-duplex equilibria, were systematically eliminated. A classic line-broadening mechanism in solution-state NMR is chemical exchange. Assuming chemical exchange in the form of conformational dynamics (e.g., oscillation of the purine base about the glycosidic torsion angle), 500-MHz ^1H $T_{1\rho}$ and 2D-NOESY data were used to constrain the correlation time of the internal motion to a range between the T_1 and $T_{1\rho}$ minima. Calculated lineshapes using a two-site exchange model indicate that motion with a τ_c of ca. $1.0 \times 10^{-5} \text{ sec rad}^{-1}$ to $1.6 \times 10^{-4} \text{ sec rad}^{-1}$ is the probable cause of the observed line broadening. The broadening thus

Figure 3.2. The 500-MHz ^1H spectra at 31°C of the aromatic region in A) $[\text{d}(\text{GCCGTTAACGGC})]_2$ with the adenine H2 resonances labeled A7 and A8. The A7-H8 and A8-H8 resonances are labeled. (Note: The apparent 2:1 ratio of H2:H8 peak areas reflects exchange of the C8 proton by deuterium over time), and B) $[\text{d}(\text{GCCGAATTCGGC})]_2$ with the adenine H2 resonances labeled A5 and A6. The A5-H8 and A6-H8 protons are clearly labeled.

reflects changes in the angle-dependent ring-current shift from adjacent base pairs.

The physical origin of such a slow motion at the center of T_nA_n tracts might be related to the abrupt widening of the minor groove at the TpA junction observed in NMR studies, and to the unusual conformation of the adenine at the junction, which probably results from a poor base-stacking interaction between the thymine and the adenine. The combination of the two structural features may well allow the adenine at the TpA junction to experience an unusual degree of motional freedom. This motional freedom may reflect local mobility in a rigid DNA helix (i.e., oscillation about the glycosidic bond) or it may reflect flexibility

of the DNA helix at the TpA junction (possibly a time-dependent twist, tilt, propeller-twist, etc.) between two rigid segments of B' DNA. It may well be important to consider and/or incorporate local mobility or TpA junction flexibility into theories of DNA bending or curvature that are used to account for the quite different migration patterns of A_nT_n and T_nA_n DNA sequences in gel electrophoresis.

Structure at the TpA Junction

Complete NMR determination of the solution structure of hexadecamers will prove to be more formidable than for dodecamers. This is due not only to the spectral complexity, but also to the effects of increasingly anisotropic rotational diffusion as the length-to-diameter ratio of the DNA helix increases. For 2-D NOESY data of equal quality, meaning both signal-to-noise ratio and resolution, data interpretation is intrinsically more difficult for longer DNA duplexes because NOE crosspeak intensities in simulations can be matched to experimental intensities by adjusting either the interproton distance or the polar angle that the interproton vector subtends with the helix axis. Hence, equal quality data sets will lead to an inherently less precise structure for hexadecamers. While a complete distance-geometry structure for $[d(CGAGGTTTAAACCTCG)]_2$ is not immediately forthcoming due to a combination of the problems outlined above, J coupling data have not been shown to be affected by anisotropic diffusion and the following interesting structural features should be mentioned. In correlation spectroscopy (COSY) experiments, for all residues the $H2''$ - $H3'$ couplings are unobservable and the $H1'$ - $H2'$ couplings are strong (data not shown), as expected for B-DNA.⁽¹⁰⁾ However, from an analysis of the $H3'$ to $H4'$ region of the 500-MHz 1H DQF-COSY spectrum shown in Figure 3.3, only two of the furanose sugar rings assume a C2'-endo conformation (i.e., exhibit very weak $J_{3',4'}$ couplings). These two sugars correspond to the first purine of the two purine runs in $[d(CGAGGTTTAAACCTCG)]_2$, namely, G2 in the GAGG tract and A9 in the AAA tract. In the AAA fragment, A10 has an intermediate crosspeak intensity and the intensity of A11 is strong; in the CAGG fragment, A3 and G4 have intermediate crosspeak intensities while the intensity of G6 is strong. These data indicate that the sugar conformation undergoes a progressive transition to lower pseudorotation phase angles (P) in the 5' to 3' direction in both the AAA and GAGG tracts (i.e., from 2'-endo ($P \approx 126^\circ$) at G2 and A9 to around 1'-exo ($P \approx 126^\circ$) at

Figure 3.3. The $H3'$ - $H4'$ region of the 500-MHz 1H DQF-COSY spectrum of $[d(CGAGGTTTAAACCTCG)]_2$ at $31^\circ C$.

G5 and A11, respectively). All other $H3'$ - $H4'$ DQF-COSY crosspeak intensities are readily detectable indicating that the remaining sugars all assume a structure that is closer to the C1'-exo conformation than to the C2'-endo conformation. The gradual 2'-endo to 1'-exo transition in purine tracts may or may not be related to the reduced minor groove width at the outside edges of the T_nA_n tract (strong(n) $H2$ to (m+1) $H1'$ NOEs) and the unusual structure at the TpA central junction. It is worth noting that while the $J_{3',4'}$ couplings tend to increase along the T_3 tract in the 5' to 3' direction, being strongest (lowest P value) at T8, there is a striking difference in sugar conformation between T8 (high J, low P) and A9 (low J, high P) at the TpA step, which is most certainly diagnostic of the unusual structure of the TpA junction. The dramatic difference in sugar conformation at the TpA junction is likely the result of poor base-stacking at the TpA step₍₁₁₎ rather than the cause of the distortion.

Finally, it is interesting that the family of restriction enzymes that specifically recognize T_nA_n fragments of DNA (e.g., Dra I, Pme I, and Hpa I, all cleave the phosphodiester bond in the backbone precisely at the TpA junction). Mobility, coupled to distinct structural features, such as base-stacking or sugar conformations

characteristic of the TpA junction, may play a role in protein-DNA recognition and in accessing the conformation required for hydrolysis of this phosphodiester bond.

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4. Applications of Solid-State NMR to Analysis of Adsorbate Chemistry

H. P. Cho

Projects using solid-state NMR can be divided into two general categories: 1) the application of magnetic resonance methods to chemical and materials problems arising in environmental science, and 2) the development of novel techniques, experiments, and instrumentation for the study of fundamental processes by NMR spectroscopy.

Three classes of systems that are of current concern regarding the application of NMR methods are geological samples, molecular sieve compounds, and simulated and actual toxic materials. The emphasis of these investigations is on obtaining results that will increase understanding of the effects of chemical and radiation exposure on the geology and geochemistry of containment areas, and provide guidance on devising prescriptions for effective remediation of sites contaminated by chemical and radiological toxins.

Developing techniques and instrumentation to increase sensitivity, resolution, and information content of NMR spectra are being explored with an emphasis on analytical procedures that enlarge the scope of NMR and lead to new approaches to solving the problems of chemical and radiological contamination.

Organic Adsorbates in Zeolites

The distribution, location, and dynamics of small organic molecules residing within the pores of zeolites are being probed by proton, carbon-13, and deuterium NMR spectroscopy.^(1,2) The data obtained in this study provide a picture of host-adsorbate interactions that can be used to direct the synthesis of zeolites with improved structural, catalytic, and sieving properties, and to determine conditions that optimize the performance of zeolites in several of their common applications. Multinuclear NMR is a

unique and especially effective method for this kind of study, since it offers perspectives on a variety of diverse aspects of *in situ* adsorbate chemistry, in the absence of signal interference from the zeolite framework itself. The demonstration of novel experimental schemes that expand upon this versatility and specificity, such as multiple-quantum NMR, variable temperature studies, and spinning techniques, is a parallel effort of this project.

The impetus for this study derives from the fact that the interaction of organic adsorbates with zeolite hosts can have several significant consequences for the zeolite structure and function. The synthesis of some zeolites, for example, is directed with extreme specificity by an obligatory organic template molecule, usually a crown ether, which becomes trapped within the zeolite lattice. In other settings, such as separations or catalytic processes, organics are introduced to the already formed zeolite lattice as guest molecules, where they may undergo catalyzed reactions or be filtered. Common, fundamental questions on the disposition of the adsorbate are posed by all these systems, for example, on the movement of adsorbate both within a cage and from cage to cage, on the distribution of guest molecules within the host, and on the placement of the adsorbate when trapped inside a given cage.

Several representative zeolites have been analyzed, including zeolites where the adsorbate is a template used in the synthesis, and zeolites where the adsorbate has been introduced through postsynthesis impregnation of the host. The results of carbon-13 NMR, Raman spectroscopy, thermal gravimetric analysis, and other analytical methods confirm the presence of intact adsorbates within intact hosts, and reveal a range of molecular distributions and different trajectories for motion. Additional data can be interpreted to determine molecule distribution also, as for hexamethylbenzene, where the distribution of organics illustrated on the right in Figure 4.1 is indicated, with two molecules per cage even at low cage:adsorbate ratios.

Water in Nominally Anhydrous Minerals

Infrared absorption spectroscopy and proton NMR spectroscopy are being utilized to further understanding of the role and incorporation of stoichiometric water in silicate minerals.⁽³⁾ This research is motivated by the observation that numerous physical, mechanical, and electrical properties of common, nominally anhydrous minerals can be significantly

Figure 4.1. Schematic diagrams of possible hexamethylbenzene spatial distributions within the supercages of a single NaY zeolite crystallite for different bulk concentrations of organic molecules. The open circles represent empty supercages, and solid circles the supercages containing two hexamethylbenzene molecules.

altered by the presence of minute amounts of water. Because of this sensitivity to water, the results of this work have potentially important implications for radioactive and chemical waste storage site selection, as well as for more fundamental geochemical questions on conditions inside the earth's mantle where the minerals are formed.

The isotope selectivity of proton NMR makes this technique an ideal vehicle for focusing on rare water molecules to the exclusion of the bulk material. Figure 4.2 shows a series of proton multiple-quantum NMR spectra for a grossular garnet from Kenya. The observation of only +1-quantum lines in these spectra is conclusive evidence that protons occur as well-isolated pairs within the host lattice. Further analyses of

Figure 4.2. Multiple-quantum NMR magnitude spectra of a Kenyan grossular garnet as a function of increasing preparation period time.

proton NMR spectra reveal that the separation of protons within a pair is approximately 1.69 Å, somewhat larger than the value of 1.59 Å typically associated with proton pairs on water molecules of hydrated inorganic crystals.

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5. The Use of Gas Phase H/D Isotopic Exchange Reactions to Probe the Structure of Protein Ions in the Gas Phase

B. E. Winger, K. J. Light-Wahl, and R. D. Smith

New methods to probe the higher order structure of large molecules can potentially provide qualitative information on changes to the 3-D structure of important biomolecules using far less sample than currently required with existing methods. With the recent development of "soft" ionization methods based upon electrospray ionization (ESI),^(1,2) allowing the formation of multiply charged ions from large polypeptides and proteins, new opportunities for probing structural characteristics and reactivity have arisen. Previous studies of multiply protonated cytochrome *c* reactions with dimethylamine⁽³⁾ and 1,6-diaminohexane⁽⁴⁾ in a quadrupole ion trap mass spectrometer, for example, have shown differences in the reactivity of various charge states. Chait and coworkers have also shown that H/D isotopic exchange with D₂O in solution can be useful for qualitatively probing protein structure.⁽⁵⁾ Recent reports indicate that various noncovalent associations, and perhaps elements of higher order structure of macromolecular ions, may be preserved in the gas phase after ESI.⁽⁶⁾ The method we have developed invokes the use of thermal energy ion/molecule reactions of multiply protonated proteins with D₂O to probe higher order gas-phase structural differences.

In our studies, multiply protonated protein molecules formed via ESI are transported in the gas phase through a dual "inlet/reaction" capillary interface, developed at PNL.⁽⁷⁾ The first (inlet) capillary is temperature-regulated to assist droplet evaporation and ion desolvation. At the junction with the second capillary, D₂O (or H₂O) gas is added, and subsequent thermal energy reactions between the partially or completely desolvated ions occur in a second temperature-regulated capillary before expansion into vacuum. The extent of deuterium isotopic exchange is determined from the change in

molecular weight measured with a triple quadrupole mass spectrometer.^(2,7) Figure 5.1 shows a comparison of mass spectra for the protein cytochrome *c*, and the shift in molecular ion m/z , which results from H/D exchange.

The rate of H/D exchange for the individual proteins is dependent upon the reaction temperature. The data shown were obtained with the reaction capillary at 145°C, above which temperature thermally induced dissociation⁽⁸⁾ increases for the reduced species. When multiply protonated molecules generated through ESI from native bovine proinsulin react with gas-phase D_2O , the measured average molecular mass (M_r) calculated from the ESI m/z spectrum is 8715.0 ± 1.4 Da, which is 33.2 Da higher than the nondeuterated molecule (M_r 8681.8 $\pm$ 1.4 Da). This corresponds to approximately 25.2% deuterium incorporation (based on 132 potentially labile hydrogens in the native molecule). Upon reduction of the three disulfide bonds in proinsulin with 1,4-dithiothreitol, the number of potentially labile hydrogens increases to 138 and the measured M_r to 8687.8 ± 1.4 Da. However, when this species is electrosprayed and allowed to react with gas-phase D_2O , the measured M_r is 8705.2 ± 1.4 Da. This corresponds to an increase in M_r of only 17.4 Da, or approximately 12.6% deuterium incorporation for the reduced proinsulin ions. Therefore, the ratio of the difference in molecular weight after reaction with D_2O for the native (N) and reduced (R) proteins, $\Delta N/\Delta R$, is 1.91 ± 0.25 , after accounting for the M_r change due to the reduction of three disulfide bonds.

Figure 5.1. Comparison of ESI mass spectra for cytochrome *c* (a) and after reactions with large partial pressures of H_2O (b) and D_2O (c).

Comparison of H/D exchange observed for the native and reduced protein ions of the same charge state shows ions formed from the native protein are more reactive than the reduced form. The charge state distribution observed in the ESI m/z spectrum for native proinsulin consists primarily of the 7⁺ and 8⁺ charge states, while the distribution observed for the reduced proinsulin ranges from 7⁺ to 11⁺. Upon reaction with D_2O (or H_2O), the only charge state observed for the native protein is 7⁺, while the charge states 7⁺ to 9⁺ are observed for the reduced proteins. While it is not possible to determine whether the extent of H/D exchange differs for the two initial charge states of the native protein, no significant difference is observed for the limited number of product charge states after reaction of the reduced protein.

To investigate whether $\Delta N/\Delta R$ is also dependent on the reaction temperature, the same reactions were performed at 120°C, and the value of $\Delta N/\Delta R$ was determined to be 1.87 ± 0.25 . This suggests that, unlike the total exchange rate, the relative H/D exchange rate is not strongly temperature dependent over the range subject to investigation (typically 90° to 150°C). Table 5.1 summarizes these results as well as those obtained for the native and reduced forms of α -lactalbumin at 120°C where a smaller but still significant $\Delta N/\Delta R$ ratio of 1.18 ± 0.06 was observed. These data show that gas-phase ions formed from these proteins exhibit opposite behavior toward H/D exchange than observed in solution⁽⁵⁾ where the denatured or reduced form is more reactive, presumably due to a more accessible solution structure.

The present results show that qualitative differences in gas-phase structure of multiply charged macromolecules can be probed using high-pressure ion/molecule reactions. We speculate currently that the greater H/D exchange for the ions formed from native disulfide-bonded protein is due to coulombic contributions,⁽⁵⁾ arising from the more compact gas-phase structure. Other recent studies (see Section 6) have shown that gas-phase proton transfer reactions of multiply protonated proteins with diethylamine exhibit higher reactivity with ions formed from the native protein as compared to ions from the reduced form having the same charge state: a similar trend to that observed here. Possible coulombic contributions to enhanced proton transfer efficiency for highly charged ions have been noted.^(3,4,7) It is reasonable that the gas-phase structure of the constrained disulfide-bonded protein will result in enhanced coulombic effects compared to the disulfide reduced form. As a consequence,

Table 5.1. Experimentally determined average molecular weight M_r for the native and reduced forms of the proteins bovine proinsulin and α -lactalbumin after reaction with D_2O and % H/D exchange. Also included is $\Delta N/\Delta R$, the ratio of the difference in molecular weight after reaction with D_2O for the native and reduced forms of the protein.

	<u>M_r after D_2O Reaction</u>	<u>% H/D exchange</u>	<u>$\Delta N/\Delta R$</u>
Native Proinsulin (120°C) ^a	8,703.8±1.4	16.7	1.87±0.25
Reduced Proinsulin (120°C) ^b	8,699.6±1.4	8.9	
Native Proinsulin (145°C) ^a	8,715.0±1.4	25.2	1.91±0.25
Reduced Proinsulin (145°C) ^b	8,705.2±1.4	12.6	
Native α -lactalbumin (120°C) ^c	14,277.0±2.2	44.8	1.18±0.06
Reduced α -lactalbumin (120°C) ^d	14,269.6±2.2	36.9	
^a M_r = 8,681.8	^b M_r = 8,687.8	^c M_r = 14,175.2	^d M_r = 14,183.0

this increase in coulombic energy may be sufficiently large to assist in overcoming reaction barriers, resulting in increased reactivity (e.g., H/D exchange, proton transfer, etc.) depending upon gas-phase structure and charge location.

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6. Studies of Coulombic Effects on the Dissociation of Macromolecular Ions

A. L. Rockwood, M. Busman,
and R. D. Smith

The demonstration of extensive multiple charging of large ions in electrospray ionization mass spectrometry (ESI-MS)⁽¹⁾ has introduced a new type of chemical species to gas-phase chemistry. Ions as large as 2,000,000 dalton with more than 1000 charges have been reported.⁽¹⁾ Little is known about the chemical characteristics (e.g., structure, reactivity) of these ions, and particularly the dependence of chemical characteristics upon the ion's extent of charging.⁽²⁾ The properties of such chemical species are, in themselves, fundamentally interesting. Furthermore, greater knowledge about these extensively charged ions would be of great use for the interpretation of ESI-MS results,⁽³⁾ as well as for understanding the properties of these ions, such as coulombic effects in their dissociation.⁽⁴⁾ Our laboratory has been extensively involved in the study of the dissociation of large multiply charged ions by collisional activation.^(5,6,7)

Stabilities of the ions can, in principle, be evaluated in terms of activation energies required for fragmentation. The electrospray process is well suited for this type of evaluation, as it produces ions at atmospheric pressure, where they are rapidly thermalized to ambient temperatures. We have developed methods to study the thermal activation of electrosprayed ions using a heated capillary reactor. In this heated capillary reactor ions are all heated to the same, well characterizable temperature. This is in contrast to other commonly used activation methods in MS, in which temperature is not very well known. The design of the reactor makes it well suited for studies of gas-phase kinetics of ions produced at high pressures. The present measurements provide new insight into the role of coulombic forces upon the stability of large, multiply charged ions.⁽⁴⁾

Ion currents for four charge states of multiply protonated molecular ions of melittin were produced by ESI, and recorded as a function of the capillary temperature. An important result of these experiments is the finding of reduced stabilities of the more highly charged ions. The plots in Figure 6.1 show the attenuation of ion current for the parent ions as a function of temperature. It is easily seen that the high-charge states of melittin are attenuated at lower temperatures than low-charge states. The calculated activation

Figure 6.1. Representative plots of molecular ion current versus temperature for the 3+, 4+, 5+ and 6+ charge states of melittin.

energies (E_a) are given in Table 6.1. The differences in activation energies for different charge states correspond to a few tenths of an eV, and the trends appear related primarily to differences in activation energy, perhaps modified slightly by entropic effects.

The activation energies determined in this work approach the bond energy of a covalent bond. It is clear that the major processes leading to loss of molecular ions involve dissociation by cleavage of peptide bonds, since known fragment ions (e.g., y_{13}^2 , y_{13}^3) are observed, which is consistent with previous mass spectrometric studies.⁽³⁾ The reduction of the activation energies for the highly charged polypeptide ions qualitatively supports a role of coulombic energy in their destabilization. Indeed, the magnitude of the activation energy lowering is similar to that predicted on the basis of simple models we have developed previously.⁽⁴⁾

Perhaps more importantly, these studies point the way toward techniques for kinetic studies of gas-phase ions under well characterizable conditions of temperature and reaction time. This will provide a basis for the determination of such fundamental ion properties as bond dissociation energies. This technique should be

Table 6.1. Attenuation Temperatures and Activation Energies for Multiply Protonated Melittin

Charge State	$T_{1/2}$ (K)	$T_{1/2}/T_{1/2,+5}$	E_a (kJ/mol)
3+	650	1.210	170
4+	590	1.099	154
5+	537	1	141
6+	515	0.959	135

applicable to any method capable of generating ions at atmospheric pressure, and is not limited to electrospray-generated ions. Further refinement of the present apparatus should vastly improve the quality of the measurements, as well as broaden the scope of application. For example, development of improved temperature control and temperature measurement, as well as methods for varying residence time, is presently being pursued. Furthermore, the technique could be adapted to study the kinetics of ion-molecule and ion-ion reactions. Another attractive feature is that the range of application is not limited by molecular ion m/z , as is the case for conventional collisional activation in which, for a given ionic charge, the efficiency of activation decreases as the mass of the ion increases.

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7. Development of Methods and Instrumentation for Capillary Electrophoresis - Mass Spectrometry

R. D. Smith, H. R. Udseth, J. H. Wahl, and D. R. Goodlett

The history of analytical advances in MS has highlighted the special importance of the combination of separation methods having high selectivity and resolving power in conjunction with the high sensitivity and specificity of mass spectrometric detection. "Real-world" samples are invariably mixtures and are often very complex. Any useful analytical methods must accommodate contributions from the sample matrix, interfering substances, and other factors that may influence the analysis. The dynamic combination of capillary electrophoresis (CE), a separation method of high efficiency, speed, and flexibility, with ESI-MS is thus particularly advantageous.

The online combination of capillary zone electrophoresis (CZE), one form of CE, with ESI-MS was developed at PNL.⁽¹⁾ Subsequently, a liquid sheath-electrode interface was developed from which the solvent composition and flow rate of the electrosprayed liquid could be controlled independently of the CZE buffer (which is desirable since high-percentage aqueous and high-ionic strength buffers that are useful in CZE are not well tolerated by ESI).⁽¹⁾ The interface provides greatly improved interface stability and performance and is adaptable to other forms of CE. Because CE relies on analyte charge in solution and the ESI process is nearly universal for charged species, the CE/ESI-MS combination is highly complementary. Thus, the CZE/MS approach offers previously unobtainable separation efficiencies (for the combination with MS) as well as detection limits that can greatly surpass existing methods.^(2,3,4,5)

One reason for the current interest in CE-MS techniques is for identification and analysis of DNA adducts with extremely low levels of modified DNA resulting from chemical modification or radiation damage. This is an important but formidable analytical challenge due to the extremely low concentrations at environmental levels of exposure. Ideally, the objective is to not only detect "known" compounds, but to determine the structure of unknown DNA adducts with sample sizes far too small to be addressed by other analytical methods. This provides the essential tool for understanding the origin of

health effects after exposure at the molecular level. These objectives directed our interest in CE, ESI-MS, and ESI-MS/MS. In fact, it can be argued that the CE-MS/MS combination obtained using the ESI interface should provide a near-ideal analytical approach for DNA adducts.

Some of the most interesting and difficult applications require techniques that are capable of analyses on the single-cell level, where the maximum amounts of components are at the attomole level and below. In general, the analytical methodology being developed for such demanding assays incorporate a separation technique with a sensitive, selective, and broadly applicable detection method. Presently, techniques such as laser-induced fluorescence^(2,4) and electrochemical detection have provided the most impressive sensitivities demonstrated with CE. Unfortunately, these detection techniques are limited because compound identification is generally based on electrophoretic mobilities. For more demanding applications, MS has not normally been considered an adequately sensitive technique, particularly for biopolymer characterization. The advantage, however, of MS detection schemes are that component identification and accurate molecular weight information can be determined, even for proteins.

In the past year, we have developed a new "micro-spray" ESI interface that has provided a large gain in sensitivity. Figure 7.1 shows a CE-MS separation

Figure 7.1. Reconstructed single-ion electropherograms for ions representative of three proteins separated in a 20- μ m inside diameter capillary.

of a simple pentapeptide mixture, demonstrating the attomole-level sensitivity obtainable with the "microspray" dance. We have also explored new methods for enhancing the sensitivity of ESI-MS when combined with CE separations. We have shown that the use of small diameter capillaries can significantly boost ESI sensitivity by providing a near ideal match of analyte and ESI capabilities. Figure 7.2 shows reconstructed single-ion electropherograms obtained during a CE-MS separation using full scan detection. The separation was conducted in a 5- μ m-diameter capillary and ~600 attomoles of each protein were injected. Mass spectra were obtained from each component with sufficient quality to allow accurate molecular weight determination.

In addition to the above, a new reduced elution speed (RES) concept for CE-MS has been developed and demonstrated. The method was implemented by instituting a step change in the CE electric field strength

Figure 7.2. Mass spectra for proteins obtained from an injection of 600 attomoles of protein into a 5- μ m capillary for CE-MS analysis.

for desired periods of time during a separation. As a result, the m/z range that can be scanned while a solute elutes from the capillary is increased by a factor proportional to the decrease in CE electric field strength. Under conditions where the quantity of solute entering the ESI source per unit of time exceeds the current available for ionization of all solute molecules present (i.e., solute saturates the electrospray process), we expect no substantial decrease in maximum ion intensity when the electric field strength is decreased. Thus, a larger fraction of the analyte will be transferred to the gas phase as ions during RES CE-MS than during constant electric field strength CE-MS.

Figure 7.3A shows the total ion electropherogram for the separation of 60 fmoles (injected) each of carbonic anhydrase B, aprotinin, myoglobin, and cytochrome *c* using a constant electric field strength of 300 V/cm during CE-ESI/MS. In comparison, Figure 7.3B shows the total ion electropherogram (TIE) for the same mixture where the electric field strength was reduced to 60 V/cm one minute before migration of the first protein into the ESI source. The insert of Figure 7.3B shows the same total ion electropherogram after the abscissa has been compressed by a factor of five. The prolonged residence time of solute in the electrospray can be exploited in several ways including 1) an increase in the m/z range scanned, 2) an increase in the number of scans recorded during elution of a given solute, and 3) an enhancement of sensitivity (integrated ion intensity) for a given solute. The method does not increase solute consumption, allows sensitivities for peptide and protein analyses extending into the low femtomole regime, and incurs very little loss in ion intensity, particularly important for MS/MS methods and their potential application to peptide sequencing.

These results represent encouraging progress toward the goal of ultrasensitive peptide and protein analysis at low attomole and subattomole levels. A number of methodological problems, however, remain to be addressed. For example, improvements in methods to chemically modify the inner surface of the capillary, which will provide a more complete coverage and enhanced separation quality, remain a fundamental challenge. Improved procedures for sample and buffer preparation and handling are also needed to prevent capillary plugging, a common problem with small ID capillaries. In addition, the ESI interface sensitivity may be improved further because the efficiency of ion transport from the ESI source, which is

Figure 7.3. Comparison of constant field strength (A) and reduced elution speed (B) CE/ESI-MS analysis of a mixture containing carbonic anhydrase, aprotinin, myoglobin and cytochrome *c*. The constant field strength CE/ESI-MS analysis was conducted at 300 V/cm. The reduced elution speed CE/ESI-MS analysis was conducted at 300 V/cm until one minute before elution of the first protein when the electric field strength was reduced to 60 V/cm.

at atmospheric pressure, to the MS detector remains relatively low. Possible mechanisms for improved ESI performance may involve enrichment for large ions relative to small ions for MS transmission due to beam dynamic effects (i.e., improved focusing of the heaving analyte ions during gas expansion into vacuum) or a reduction in space charge effects arising in the electrospray plume due to a reduced ESI current with the smaller ID capillaries. Preliminary studies suggest that the latter may account for as much as a 10^2 gain in ion transmission efficiency. Solute sensitivity can be improved further by the use of array detectors, and potentially with ion trapping and TOF mass spectrometers for broad m/z range detection. These developments may also alleviate the reduced dynamic range resulting from the

smaller ESI currents when using small ID capillaries. A coalescence of these methods holds the potential of CE-ESI/MS at zeptomole (10^{-21} mole) levels.

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8. The Study of Noncovalent Associations in Solution by Mass Spectrometry

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Electrospray ionization has been demonstrated to be a "soft" ionization technique, allowing accurate molecular weight determination for biopolymers due to gas-phase multiple charging.⁽¹⁾ This laboratory and others have demonstrated that noncovalent associations can be preserved into the gas phase with ESI, providing a new approach to the determination of both nonspecific⁽²⁾ and structurally specific⁽³⁾ noncovalent associations in solution. The mass spectrometric experimental conditions necessary to preserve such noncovalent associations and physical constraints upon such associations have yet to be well elucidated, although it is clear that gentle interface conditions minimizing internal excitation of noncovalent complexes are helpful. Base-paired oligonucleotide hybridization constitutes one of the most important and thoroughly studied noncovalent associations of biopolymers. Our initial attempts to observe duplex oligonucleotides resulted in detection of only the monomeric constituents. In 1992, we suc-

ceeded in developments that are appropriate for the ionization of intact duplex oligonucleotides and detection by negative ion ESI-MS.

As a model system, two complementary 20-base single-stranded oligonucleotides were prepared with a DNA synthesizer by phosphoramidite chemistry. The samples were purified by reversed-phase high performance liquid chromatography (HPLC) and ultrafiltration to remove residual salt impurities. Oligonucleotide I contained pyrimidine bases with the sequence 5'-dCCTTCCTCCCTCTCTCCTCC-3' (M_r 5826.9), and oligonucleotide II was composed of the complementary purine bases with the sequence 5'-dGGAGGAGAGAGGGAGGAAGG-3' (M_r 6410.3), chosen to minimize ambiguous association of the complementary single strands. Also, their significant differences in M_r allowed potential nonspecific self association to be resolved under the low-resolution MS studies employed. The purity of the single strands was confirmed by MS and their concentrations were determined by UV spectrophotometry. The single-stranded oligonucleotides (1×10^{-4} M) were annealed in 10 mM NH_4OAc by heating to $90^\circ\text{--}100^\circ\text{C}$ for five minutes then slowly cooled to room temperature over three hours. Negative ion ESI mass spectra were obtained using a new extended m/z range ($\sim 45,000$) quadrupole mass spectrometer developed in our laboratory employing a heated capillary interface.⁽⁴⁾ Mass spectra were obtained under conditions intended to minimize heating of molecular ions (i.e., low interface voltage, low capillary temperature), but still providing sufficient excitation to desolvate the highly solvated droplets. Figure 8.1 shows a low resolution mass spectrum of the hybridized sample showing multiply charged ions (D^{8-} to D^{2-}) corresponding to the intact duplex (D) dominating at $\sim m/z$ 2500. It is noteworthy that while both single stranded constituents (I and II) are observed at low m/z , the duplex form is predominant at higher m/z . The insert in Figure 8.1 shows an expansion of the m/z region of the 5⁻ charge state of the double-stranded duplex ion (D^{5-}) at m/z 2446 corresponding to the specific hybridization of the complementary single-stranded species (I + II). Homodimeric association of each strand would be expected to produce additional 5⁻ ions at m/z 2330 (I + I) and m/z 2563 (II + II) that are not observed, indicating that a more specific association was involved in producing the duplex ions. In addition, the intact duplex was not observed when distilled deionized water was substituted as the solvent. The measured molecular weights for the individual species of 5827 ± 2 Da (I)

Figure 8.1. Negative ion electrospray ionization mass spectrum of a 20-mer oligodeoxyribonucleotide duplex. Peaks labeled D are from the duplex ions and I, II are from the indicated charge states of the complementary single-stranded ions. The insert shows the 5⁻ charge state region of the hybrid duplex ion at m/z 2446, and the absence of the nonspecific association ions (I + I)⁵⁻ at m/z 2330 and (II + II)⁵⁻ at m/z 2563.

and 6410 ± 2 Da (II) were consistent with the sequence within experimental uncertainty. The measured molecular weight of the duplex (12297 ± 10 Da) is higher than that calculated (M_r 12237.1). This may be the result of insufficient desolvation of these higher molecular weight, lower charge state ions compared to their single-stranded counterparts, or to greater counterion association (e.g., residual Na^+ , NH_4^+ , etc., which may remain and indeed may be necessary to stabilize the duplex structure in the gas phase).

The present results are the first observation of duplex oligonucleotides from solution by MS, a potentially significant first step towards the study of oligonucleotide and nucleic acid associations. The results show that careful choice of both solution and ESI-MS interface conditions are crucial. An extended m/z range may also be useful for such observations since the intact duplex is observed with significant intensity only in relatively low-charge states. It is uncertain whether the monomeric constituents observed in the mass spectra are representative of the solution, or if they are products of dissociation of coulombically destabilized higher charge states of the duplex.

Indeed, one expects decreased stability for the gas-phase duplex in higher charge states as desolvation removes the dielectric shielding provided by the solvent.

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9. Analysis of Covalent Modifications of Proteins by Electrospray Ionization-Mass Spectrometry

C. G. Edmonds, A. F. Fuciarelli, B. T. Thrall, and D. L. Springer

Electrospray ionization mass spectrometry^(1,2) provides powerful insight into the structure of intact proteins and their enzymatically derived peptides.^(3,4) The ESI affords a distribution of multiply charged molecular ions, which may be analyzed by conventional quadrupole mass analyzers ($M/\Delta M$ 1000), for example, to determine mass with a precision ($\pm 0.01\%$) substantially better than conventional biochemical

techniques. The elucidation of primary structure of unknown proteins is one important area of application. Additionally, where the primary structure of the analyte is constrained (e.g., among mutant protein species) or where a known structure has been subjected to chemical or natural post-translational transformations, this technique provides an extraordinarily sensitive and selective probe of the nature and extent of these modifications. For example, acrylamide adducted hemoglobin (Hb) subunits and the products of proteolytic digestion may be directly analyzed by ESI-MS with potential application as a biomarker of occupational exposure. Similarly, the radiation-induced modifications and the natural post-translational modifications of histone proteins may be studied. Results of our initial studies are outlined in this section. Hemoglobin adducts have been used to monitor occupational exposure to a number of compounds. Until recently the most common procedure to identify and characterize Hb adducts has been to cleave the adduct from the protein and derivatize and characterize it by gas chromatography-mass spectrometry (GC-MS). To extend these approaches, we examined acrylamide-adducted Hb using ESI-MS in an attempt to identify the adducting moiety as well as to obtain information on the amino acid residues involved. Carbon-14 acrylamide and purified human Hb (type Ao) were incubated under conditions that yielded high adduct levels. The ESI-MS analysis of the intact HPLC-separated subunits indicated distinct differences in the ion profiles for the adducted and nonadducted species. Mass spectra of the intact β -subunit demonstrated three distinct mass increments of approximately 71, 101, and 136 Da, as is seen in Figure 9.1. The ESI-MS of HPLC-purified fractions of the V8 proteinase digestion localizes the first of these on the peptide bearing Cys-93 (V91-101). The measured mass increment for this species is consistent with the expected thioether derivative. The structure of the second observed adduct (incremental M_r^{Meas} 102.0 $\pm$ 1.2) is unknown but it is likewise localized on cysteine-bearing peptides, V91-101 and including V102-121, which bears Cys-112. The structure of the third adducted species is unknown and does not appear to be localized on a particular amino acid residue. Studies to confirm the cysteine residue as the location of the adducting moiety by tandem MS and to further refine the picture of acrylamide adduction in this system are in progress.

A basic subunit of chromatin structure is the nucleosome consisting of 146 base pairs of DNA wrapped around a central histone protein octamer with two

Figure 9.1. Portion of the electrospray ionization mass spectra of the products of acrylamide reaction with the β -subunit of human hemoglobin showing the $(M+18H)^{18+}$ charge state of the unchanged protein and species incremented by covalent adduction.

additional histones binding the linker regions. The histones, lysine and arginine-rich proteins, participate in this reversible complex with DNA called nucleohistone. Exposure of cellular constituents to free radicals generated with ionizing radiation results in modifications that can play a significant role in altered cellular function. Interaction of hydroxyl radicals with DNA results in modifications to base and deoxyribose moieties. In addition, hydroxyl radicals can result in generation of DNA-protein crosslinks in nucleohistone. Methodology involving acid hydrolysis of irradiated nucleohistone followed by trimethylsilylation and subsequent GC-MS has revealed the presence of DNA base-amino acid dimers.⁽⁵⁾ However, sequence information is not provided by this methodology. Application of ESI-MS to the measurement of DNA-protein crosslinks in nucleohistone provides a useful method to obtain information not available with other MS techniques.

We have conducted preliminary experiments in which ESI-MS analysis of untreated chicken erythrocyte H2B (M_r 13,789) (top Figure 9.2) and this protein exposed to 5 Gy of ionizing radiation in the presence of 100-fold molar excess of thymine (bottom Figure 9.2). The top panel of the figure shows the portion of the mass spectrum containing the $(M+20H)^{20+}$ for the following: unmodified H2B protein, a; an unknown protein, b; monoacetylated H2B, c; and artifact peaks arising from the addition of one (d, e, and f; mass increment 98 Da) and two (g; mass increment

Figure 9.2. Portions of the electrospray ionization mass spectra of untreated histone H2A (top) and this protein exposed to 5 Gy of ionizing radiation in the presence of 100-fold molar excess of thymine (bottom), showing the region containing the $(M+20H)^{20+}$ multiply charged molecular ion. Peak assignments are discussed in the text.

196 Da) noncovalent sulfate ion contaminant associations. Inspection of the mass spectrum in the same region for the treated protein reveals the same peaks plus unique peaks with measured mass increments of 126.1 Da (e, and its sulfate ion-pair peak, h), which are near the expected incremental value for thymine-H2B adduct, 125.1 Da. Additional species incremented by 140.7 Da, peaks h and i, are observed whose structure is presently unknown. Irradiation of histone H2B in the presence of excess thymine resulted in a dose-dependent increase in species with mass increments consistent with the formation of thymine adducts. The results of these experiments demonstrate the feasibility of analyzing radiation-induced modifications of histone proteins by ESI-MS.

The nature and function of covalent modifications of proteins occurring after translation and simple

proteolytic processing is a recurring theme in structural biology. In the case of histone proteins, such post-translational modifications include acetylation, methylation, phosphorylation, mono- and polyadenosine diphosphate (ADP) ribosylation and ubiquitination. The ESI-MS permits the direct analysis of the intact modified protein and the evaluation of the nature and extent of modification (Figure 9.3). Measured mass increments differ from the values predicted by the known sequence by values consistent with known acetylation and methylation post-translational modifications of histone proteins. Further experiments are being conducted to define the nature of these modifications, as well as to understand the relationship between these modifications and cellular behavior during both normal cellular replication and after insult by chemicals and radiation.

Figure 9.3. Electrospray ionization mass spectra of HPLC purified histones from chicken erythrocyte. Measured mass increments are consistent with post-translational methylation and acetylation of these proteins.

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10. Protein Structural Effects in Gas-Phase Ion-Molecule Reactions

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By analogy to solution phase chemistry, the reactivity of gas-phase biomolecules might be expected to depend significantly upon structure. Although it is uncertain to what extent gas-phase properties can be extrapolated from those observed in solution, and vice versa, methods that elucidate structural aspects may have significant bioanalytical and biophysical utility. An advantage of ion-molecule reactions over collisional dissociation for probing structural effects is that extensive internal excitation of the ions is not required, so the studies can be performed under conditions more likely to preserve higher order structure. These useful reactions can be transferred to any mass spectrometer.

Our ion-molecule reaction technique differs from previous work because we use much higher neutral reactant gas pressures to drive the reactions to shorter timescales, allowing examination of reactions with smaller rate constants. Thermal reaction conditions dictated by the capillary temperature allow the temperature dependence of the reaction rates to be explored using a novel capillary interface/reactor which we have recently developed.

Bovine albumin (M_r 66,430), a globular protein possessing 17 disulfide linkages, was used in testing. The ESI-MS spectrum for the native protein is shown in Figure 10.1, along with the spectrum obtained after reaction with diethylamine. Figure 10.2 shows

Figure 10.1 Electrospray ionization mass spectroscopy of native bovine albumin (M_r 66,430) (a) without, and (b) with diethylamine.

the corresponding mass spectra for the protein with its 17 disulfide linkages reduced. The nonreduced protein spectrum shifts to lower charge states than does that for the reduced protein. The highest charge state observed in positive ESI of reduced bovine albumin shifts from about 95+ before reaction to about 70+ after reaction while for native albumin, the shift is from about 63+ before reaction to 44+ after reaction.

Figure 10.2 Electrospray ionization mass spectroscopy of reduced bovine albumin (a) without, and (b) with diethylamine. Comparison with Figure 10.1 shows that much greater charge states are possible for the less structurally constrained (reduced) protein after reaction with diethylamine.

Further experiments on bovine pancreatic trypsin inhibitor aprotinin (M_r 6,512) and lysozyme (M_r 14,306) showed similar behavior. On the basis of these studies, we can conclude that the proton transfer reactivities of equally charged reduced and

nonreduced protein ions differ significantly. From the viewpoint of protein collision cross sections, the greater reactivity observed for individual charge states in the nonreduced proteins might be surprising, since the more extended structures expected for the disulfide-reduced proteins should result in larger collision cross sections. However, the proton transfer reactions relevant here occur at rates far below their collision rate. When the coulombic forces arising from charge repulsion are also considered, it seems likely that a highly charged, nonreduced protein would be more reactive than an equally charged, reduced protein, because the charge states would most likely be spaced more closely in the more constrained conformation. In such instances, the increased coulombic forces should increase the rate and exothermicity of proton transfer from multiply charged proteins.

To this point, we have considered protein conformation of two cases—native and denatured (i.e., reduced). However, our analysis has not yet incorporated the possibility that the gas-phase conformation may vary substantially with charge state. It is also possible that the ions' higher order structure may be altered by the high concentrations of amine reactant or by thermal processes during desolvation. Finally, since it is known that solution conformation can dramatically affect the pK_a s of the individual amino acid constituents of proteins, it is possible that ion-molecule chemistry could also probe higher order structural effects arising from weak (e.g., hydrogen bonding) interactions.

11. Development of Ultrahigh Resolution Electrospray Ionization-Ion Cyclotron Resonance Mass Spectrometry

R. D. Smith, S. A. Hofstadler, J. E. Bruce, and B. E. Winger

Many important applications of MS to basic and applied research demand much higher resolution than that provided by conventional mass spectrometers. Fourier Transform Ion Cyclotron Resonance (FTICR) MS offers a number of attractive features in this regard. The FTICR combines nondestructive ion detection and the capability of very high resolution. The ICR method has the capability to trap ions for an

extended time period, and allows numerous sequential m/z measurements to be conducted, a capability referred to as MSⁿ. The FTICR instrument consists of a cylindrical, cubic, or orthorhombic-shaped ion storage cell in a uniform magnetic field. Ions formed in the cell, or introduced from an external ion source can be trapped for extended time periods because of the combination of magnetic and electric fields. The ICR pressures of $\leq 10^{-9}$ torr are required for high-resolution measurements for small molecular ions.

The ICR can afford ultrahigh resolution measurements, unmatched by any other type of MS. Resolution for ICR is, to a first approximation, inversely related to m/z and proportional to magnetic field strength; very high resolution (ignoring collisional damping) can be obtained at low m/z . This is particularly relevant to ESI, where resolution for a given M_r might be expected to increase with ion charge state. In contrast to other mass spectrometric methods, both high sensitivity and high resolution can be obtained simultaneously. The development of appropriate instrumentation combining the atmospheric pressure electrospray ionization process will open broad new research opportunities by providing the basis for the formation, isolation, and extended trapping of high molecular weight biopolymers and potentially even single highly charged biopolymer molecular ions (such as DNA segments) with molecular weights extending into the mega-dalton range. These new approaches will be explored using new ESI-FTICR instrumentation developed at PNL.

The FTICR-MS has the advantage of producing ultrahigh resolution mass spectra, and can provide ultrahigh precision mass measurements. It has been recently demonstrated that coupling ESI with FTICR can produce high resolution ($> 400,000$) for proteins in excess of 12 kDa molecular weight. One factor that affects the attainable resolution in ICR is the transient lifetime, which is highly dependent upon the pressure in the FTICR cell. For larger molecules, a transient lifetime of several seconds is necessary to obtain high resolution. At higher pressures, collisions with background gas cause a dephasing of the ion packet and a rapid damping of the transient signal resulting in shorter lifetimes and lower resolution. Therefore, ultrahigh vacuum (UHV) in the analyzer cell is needed to obtain longer transient lifetimes.

Figure 11.1 gives a schematic illustration of the FTICR instrumentation. The instrumentation consists of an

ESI source interfaced to an external ion injection FTICR instrument. Key features of the instrumentation include 1) a dual-stage capillary inlet ESI source; 2) a total of six differential pumping stages that allow for operation of an atmospheric pressure ion source and an UHV analyzer region; 3) solenoid-driven mechanical shutters that block the molecular beam produced by the ESI source; 4) a unique cryobaffle located in the FTICR cell region, capable of pumping speeds for nitrogen in excess of 200,000 L/s; 5) a UHV-compatible pulsed valve used for trapping and cooling of the injected ions, as well as for collision-induced dissociation and ion-molecule reactions; and 6) a 7-tesla superconducting magnet with a highly homogeneous magnetic field. With this system, an ESI mass spectra can be obtained for ions trapped in the ICR cell under conditions in which the effects of pressure do not degrade obtainable resolution (i.e., in the 10^{-10} torr range).

The application of ICR-MS to large proteins, DNA segments, and other large species will require obtaining high-resolution and high-mass measurement accuracy, and developing ionization methods and ion-molecule chemistry appropriate for probing specific structural feature sequencing. The high-resolution capability of ESI-FTICR for biopolymers has now been established. Figure 11.2a gives a mass spectrum obtained for bovine cytochrome c (average molecular weight = 12,231) in a 4:1 methanol:water mixture with 5% acetic acid. The charge state distribution, which ranges from 8+ to 11+, differs somewhat from ESI spectra acquired previously with

Figure 11.1 Schematic illustration of the electrospray ionization Fourier transform ion cyclotron resonance instrumentation developed at the Pacific Northwest Laboratory.

Figure 11.2 Mass spectrum for the protein cytochrome *c* obtained using Fourier transform ion cyclotron resonance. The spectrum was obtained from a single 200-msec injection and trap sequence. Figure 11.2-b shows the high resolution obtained for one charge state (the 10+ molecular ion) from this experiment, demonstrating resolution of more than 200,000.

quadrupole instrumentation. This appears to be dependent on the trapping conditions used (i.e., an energy analysis appears inherent in the trapping process). Expanding about the $(M+10H)^{10+}$ ion, one observes the isotopic distribution for the molecular species of a particular charge state illustrated in Figure 11.2b. The measured mass resolution, $m/\Delta m$, is 111,000 with a full apodization applied to the transient, while the unapodized transient yields a resolution of 204,000. More recent results have shown resolutions as high as 400,000 obtainable at 10^{-9} torr ICR cell pressure, but routine use requires the ability to handle longer transients (due to current data system limitations). These initial results confirm our expectation that FTICR methods with ESI will provide a new capability for characterization and structural studies of large molecular species.^(1,2)

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Materials and Interfaces

Materials and Interfaces

The basic science issues underlying the chemical and physical processes that control the development of advanced processes for waste remediation, the dynamics of contaminants in waste tanks and the subsurface environment, and the development of modern chemical sensors are remarkably similar. The recognition of this common science base is a cornerstone of the research undertaken in the MSRC, and is reflected in the organization of the Materials and Interfaces program. Four research groups—Chemical Sensors, Surface Chemistry, Materials Synthesis, and Interphase Chemistry—comprise this program. The precisely controlled design of materials by research epitaxy, electrochemical synthesis, or bulk sol-gel processes is supported by advanced surface characterization techniques. The Interphase Chemistry group is being formed in recognition of the fact that real remediation processes, or chemical sensing, occur in complex, heterogeneous environments. The scientific activity of this group will form a true scientific base for technological solutions to environmental management by incorporating information from the microscopic through the macroscopic scale. Finally, the fundamental understanding of interfacial and interphasial interactions that emerges will be incorporated into a chemical sensor design and testing program.

Staffing was our major goal in 1992. Dr. Jiri Janata, the Associate Director for Materials and Interfaces arrived in January, and several senior staff members arrived in late summer. Dr. Scott Chambers, formerly of the Boeing High Technology Center, became the technical group leader (TGL) for the Materials Synthesis Group. His expertise is in research epitaxy and surface science. Dr. Mira Josowicz focuses on applied electrochemistry and electrochemical synthesis of sensing materials. The Surface Science technical group has two senior members: Dr. Chuck Peden, who is the TGL, and Dr. Mike Henderson. Their interests are in the areas of surface chemistry and catalysis of oxide and mineral surfaces using advanced surface science probes. The Interphase Chemistry technical group has one junior scientist, Dr. Cindy Bruckner-Lea. Her expertise is in the interphasial chemistry of organized layers. The Chemical Sensor TGL is Dr. Jay W. Grate, who specializes in the design of selective layers for gas sensors and the development of sensor arrays.

Dr. Barry Wise at PNL, formerly with the Waste Technology Center, has a strong expertise in the characterization of complex waste systems. Dr. Wise's scientific expertise is in chemometrics. Dr. John LaFemina is the Materials and Interfaces program manager and also provides expertise and support in materials theory. Glenn Dunham, a technical specialist, provides technical support for the growing instrumentation base. His expertise is in physics, instrumentation, and the growth of materials. Finally, the Materials and Interfaces program maintains strong interaction with the other research programs of the MSRC and PNL.

The research staff has also received recognition from the international scientific community during the past year. Dr. Janata was a finalist in the international "Science pour l'Art" competition sponsored by the French firm Moët Hennessy-Louis Vuitton Inc. Dr. Janata was also asked to serve on the Scientific Committee of the Institute for Environmental Technology in Berlin. The Institute for Environmental Technology is considered to be the German counterpart to the EMSL.

Dr. LaFemina was named the Series Editor for *The Chemistry and Physics of Surfaces and Interfaces*, a new series of books to be published by CRC Press. Dr. Wise was appointed Adjunct Lecturer in Chemical Engineering at Washington State University. Several major review articles were also written, including a major review of sensor technologies by Dr. Janata,⁽¹⁾ articles on the determination of surface structure for *Surface Science Reports* by Dr. Chambers⁽²⁾ and Dr. LaFemina,⁽³⁾ and a book chapter on chemical properties in *Characterization of Metals and Alloys* by Dr. Donald Baer,⁽⁴⁾ a research collaborator from PNL's Materials and Chemical Sciences Center.

Although the staffing profile of the group is well-balanced, its research output is not. This is due to the fact that most of the staff have only recently arrived. There has been some progress, however, in the areas of mineral surface structure and chemistry, the characterization of the polymer photo-physical properties, and in the design of chemical microsensors. This research is discussed in this chapter.

1. Mineral Surface Structure and Chemistry

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A molecular level understanding of the attachments of various organic and inorganic contaminants to mineral surfaces is important for the accurate modeling of contaminant transport in the environment, as well as for determining the consequences of any environmental remediation method. For example, heavy metals are often retained in calcite rich soil layers, hence, any attempt to extract one contaminant must not end up releasing other, potentially more dangerous contaminants.

To help bring the understanding of mineral surfaces to the level achieved for metal and semiconductor surfaces, a program is being developed to examine the surface structure and chemistry of these materials. Although some materials can be readily obtained and prepared for examination, the experimental complications involved in the analysis of insulating materials, along with the preparation of well characterized surfaces, help to make mineral and oxide surfaces a significant scientific and technological challenge. Our initial work has focused on the surface structures of oxides, calcium carbonate, and metal adsorbate interactions with calcite. A new laboratory oriented toward understanding the chemistry of oxide surfaces has been completed, and a laboratory focused on preparation of oxide and mineral thin films is being established.

Calcite Surfaces

Calcite is of environmental importance both because it is a common soil constituent and it frequently interacts with groundwater contaminants. Earlier studies had shown that the transition metal cations fell into two groups, those that readily desorbed from the calcite surface, and those that tended to remain at the surface. An XPS based study of the interactions of a metal from each group (Mn and Co) has recently been published in *Surface Science*,⁽⁵⁾ and a set of XPS data from a freshly vacuum-cleaved calcite surface was included in the inaugural issue of the new *Journal Surface Science Spectra*.⁽⁶⁾

A close tie between the development of the theory of mineral surfaces and experimental studies has been one of our primary goals. During the past year *ab initio* density-functional calculations of the electronic properties of bulk calcite were performed.⁽⁷⁾ To allow comparison of the theory with experimental data, XPS valance band data and reflection electron energy loss data were collected. A comparison of the photoelectron spectra with the *ab initio* density of states is shown in Figure 1.1, and the agreement is excellent. These *ab initio* results are now being used to parameterize an empirical tight-binding, total-energy model for the computation of calcite surface and step reconstructions.

Figure 1.1 Comparison of the *ab initio* density-functional theory density of states with the XPS Valence band data.

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Oxide Surfaces

The surface structures of the cassiterite, SnO_2 , (111) and (110) surfaces are being examined by Auger spectroscopy,⁽⁸⁾ low-energy electron-diffraction (LEED) intensity analyses and by tight-binding, total-energy computations. Surface reconstructions for both surfaces have been predicted by the theory,^(9,10) and the LEED I-V data are currently being analyzed.

The (110) surface has two possible terminations, shown in Figure 1.2, for the fully relaxed surfaces. The reduced surface, shown in panel (a) of Figure 1.2, lacks the bridging oxygen atoms present at the

Figure 1.2 Ball-and-stick models of the relaxed (a) reduced and (b) stoichiometric cassiterite (SnO_2) (110) surfaces.

stoichiometric surface, shown in panel (b) of Figure 1.2. Both surfaces exhibit slight relaxations in which the surface oxygen atoms move out from the surface while the surface Sn atoms move in towards the bulk. This rumpling relaxation is characteristic of surfaces whose topology does not allow approximately bond-length conserving motions of the surface atoms. The surface atoms cannot move without significantly distorting their local bonding environment. The energy cost associated with these distortions is simply too great, hence the surfaces rumple slightly.

The (111) surface also has two possible terminations, reduced and stoichiometric. Unlike the (110) surface, however, the (111) surface topology does allow a bond-length conserving (BLC) movement of the surface atoms. Moreover, this motion also serves to reduce the dipole moment perpendicular to the surface. Preliminary tight-binding computations have indicated that the surface will relax along this BLC path. We are currently investigating the extent to which long range electrostatic interactions affect the computed relaxation by explicitly including these interactions in the tight-binding, total-energy model.

Finally, some theoretical work has been done in an effort to characterize the nature of the interatomic repulsions in these materials and the importance of including distant-neighbor interactions into models of surface structure and chemistry.^(11,12)

Environmental Materials Working Group

A small group that includes scientists from the MSRC, the Materials and Chemical Sciences Center, and the Environmental Sciences Center have been exploring areas where environmental and materials sciences overlap. Two projects initiated by this group were advanced in 1992. One project focuses on patterned nucleation of mineral phases on organic substrates.⁽¹³⁾ This effort involves cooperation with the Biomimetic Materials Growth program in the Materials and Chemical Sciences Center. The second project involves using x-ray adsorption spectroscopy (XAS) to obtain a detailed understanding of the nucleation steps starting from solution, including first adsorbed and precursor stages. These projects will aid in the understanding of waste metal/mineral codeposition processes, as well as allow for the synthesis of thin-film model mineral surfaces that may be interrogated with techniques that cannot be used on the insulating bulk materials. Figure 1.3 shows the progression of iron species from solution to thin film, as followed by XAS. The data indicate that the

Figure 1.3. Progression of iron species from solution to thin film.

hexa-coordinate solution species forms a disordered thin film of iron oxyhydroxide that is similar to goethite, -FeOOH . The data in Figure 1.3 was taken as the deposition occurred *in situ*.

2. Structural and Photophysical Properties of Polymers

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C. Frank,^(c) and J. Salley^(c)

Aromatic polyimides have found wide-ranging application in the electronics industry because of their superior thermal and mechanical properties, and their low dielectric constant. In addition, they can be etched with well defined (sub-100 nm) features following ultraviolet excitation. These polymers are also photoconductive, whether undoped or doped with electron donors, although their utility in photoconductor technologies has been limited by the low quantum yield of photogenerated conduction electrons. Experimental and theoretical examinations of PMDA-ODA (pyromellitic dianhydride-oxydianiline) polyimide have led to the conclusion that intramolecular charge transfer (ICT) from the ODA to the PMDA moiety plays an important role

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in determining the photophysical properties of the polymer films, including those germane to the intrinsic photoconduction and laser etching processes, as well as the ultraviolet absorption and emission spectra. Moreover, because the ICT is sensitive to the conformation of the polymer backbone, it can be utilized as a probe of the polymer conformation.

Our recent work in this area examined a series of isoelectronic substituted polyimides (Figure 2.1), where the structure of the polymer backbone was determined by quantum-mechanical AM1 geometry optimization, and the photophysical properties were computed using the quantum-mechanical CNDO/S3 model.⁽¹⁴⁾ An analysis of the geometric changes at the substitution site and its effect on the electronic structure enabled us to predict changes in the ICT bands of the optical absorption and emission spectra. In particular, the red-shift of the low energy ICT absorption band, shown in Figure 2.2, can be predicted by analyzing the one-electron orbitals involved in this transition.

A second organic polymer that has found widespread use in microelectronics and medical technologies is poly(ethylene terephthalate) (PET), also shown in

Figure 2.1 Schematic indication of the molecular structure of (a) substituted polyimides, and (b) poly(ethylene terephthalate).

Figure 2.2. Predicted optical absorption spectra for a series of isoelectronic aromatic polyimides.

Figure 2.1. The photophysical properties of PET, for the most part, can be understood by considering PET as a perturbed benzene system. There are, however, certain elements of the emission spectrum that arise from intermolecular (chain-chain) interactions in the amorphous regions of the polymer film.⁽¹⁵⁾ In our current work, we have used empirical molecular dynamics simulations to investigate whether single strand of PET can fold in such a way as to allow different ends of the same strand to interact. The conformational flexibility provided by the saturated ethylenic linkage certainly makes this possible. Simulations on chains of 8, 16, and 24 unit cells in length were performed and the trajectories analyzed to determine if unit cells were able to approach and strongly interact. The results of the simulations indicated that although the single PET strand did fold, into a helical conformation, unit cells

never came sufficiently close to self-interact, indicating that the anomalous emission features must be associated with regions of polymer forced into energetically unfavorable local conformations as a result of the thin-film synthesis process.

3. Chemical Sensors

J. U. Grote, J. Janata, and B. M. Wise

A major chemical sensor database that covers all aspects of chemical sensor research published during the period 1990-1991 was compiled.⁽¹⁾ A critical assessment of optical ion sensors was published,⁽¹⁶⁾ and two publications resulted from collaborative efforts. The first paper deals with a new concept of enzyme chronopotentiometry,⁽¹⁷⁾ while the second concerns an important aspect of the integrity of silicon nitride used in the fabrication of chemical microsensors.⁽¹⁸⁾

Work also continued in the area of process chemometrics, in particular, on the properties of multivariate calibration and model identification methods. This work included comparisons of non-linear biased regression methods and artificial neural networks for dynamic model identification. This is a collaborative effort with Dr. Ricker at the University of Washington and two papers dealing with the effect of biased regression on dynamic model identification are in press.^(19,20) We also worked closely with the Hanford Tank Safety Program to develop a data baseline for watchlist tanks.

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Theory, Modeling, and Simulation

Theory, Modeling, and Simulation

Theoretical and computational molecular science will play a critical role in understanding molecular processes important in restoring the environment, including understanding the migration and reactions of contaminants in soils and groundwater, developing separation processes for isolation of pollutants, developing improved materials for waste storage, understanding the enzymatic reactions involved in the biodegradation of contaminants, and understanding the interaction of hazardous chemicals with living organisms.

Modeling molecular processes that occur in the environment requires a fundamental understanding of molecules and their interaction in isolation (gas phase) and in liquids, on surfaces, and at interfaces (condensed media). The Theory, Modeling, and Simulation program contains three scientific research activities: Molecular Theory and Modeling, Materials Theory and Modeling, and Biomolecular Modeling and Simulation; and one research and development activity, Molecular Science Software. The Molecular Theory and Modeling activity focuses on understanding elementary molecular processes in both the gas and condensed phases with an emphasis on solution chemistry and the liquid-solid interface. The Materials Theory and Modeling activity extends existing theoretical models of surfaces and materials to soil minerals (oxides, carbonates, and clays), catalysts (zeolites), and polymers. The Biomolecular Modeling and Simulation activity focuses on the development and application of techniques to model biochemical systems, specifically biodegradative enzymes and proteins. The Molecular Science Software activity focuses on the development of a new generation of molecular modeling software that takes full advantage of the continuing rapid advances in computer technology, especially massively parallel computers.

The research objectives of the Theory, Modeling, and Simulation program are fourfold:

- to apply available *ab initio* techniques to study fundamental molecular processes involved in the chemistry of natural and contaminated systems
- to extend current *ab initio* techniques to treat molecular systems of future importance and to develop new techniques for addressing problems that are computationally intractable at present
- to apply available molecular modeling techniques to simulate molecular processes occurring in the multispecies, multiphase systems characteristic of natural and polluted environments
- to extend current molecular modeling techniques to treat ever more complex molecular systems and to improve the reliability and accuracy of such simulations.

The computing demands of research in the Theory, Modeling, and Simulation program are substantial and will grow dramatically over the next few years as new projects involving molecular systems of increasing size and complexity are undertaken, new staff are added to the program, and extensive collaborative projects are initiated. To provide an optimal response to the computing needs of this effort, Theory, Modeling, and Simulation, in collaboration with the Computing and Information Sciences program, will develop and manage the Molecular Science Computing Facility (MSCF) as a collaborative research facility in the EMSL. The computer hardware in the MSCF will provide state-of-the-art high performance computational and visualization capabilities for molecular simulations, while enabling the evaluation and exploitation of promising new computer technologies. The Molecular Science Software effort will provide the software needed to make maximal use of the hardware in the MSCF through research and development activities in high performance computing, graphics and visualization, and molecular databases.

1. Molecular Theory and Modeling

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Research in the Molecular Theory and Modeling program focuses on *ab initio* theoretical studies of molecular processes in isolation, in liquids, on surfaces, and at interfaces, and on developing accurate models of the complex molecular systems found in natural and contaminated environments. Applications in the program focus on five research areas: cluster chemistry, solution-phase chemistry (including supercritical fluids), separations chemistry, and interfacial chemistry. A common element in each of these focus areas is the need to understand molecular interactions in aqueous solutions or at the interface between aqueous solutions and environmentally important materials such as minerals and glasses. In addition, a small research effort is under way in the area of atmospheric chemistry. Development of new technology is concentrated in the areas of electronic structure methods and reaction rate theory.

Development of Electronic Structure Methods

Correlation Consistent Basis Sets for the Second Row Atoms (Al-Ar)

Correlation consistent and augmented correlation consistent basis sets for *ab initio* electronic structure calculations have been determined for the second row atoms (Al through Ar).⁽¹⁾ The methodology, originally developed for the first row atoms⁽²⁾ (H, B-Ne), was

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first applied to sulfur, a representative second row atom. The exponents for the even tempered sets of (*spdfg...*) correlating functions were systematically optimized for a correlated wave function (HF+1+2).

The incremental energy lowering ΔE_{corr} is the energy gained either by extending the even tempered basis set for a given symmetry by one function or by adding the first function of a higher angular symmetry to a base set. ΔE_{corr} is therefore a straightforward measure of the contribution of each basis function to the correlation energy. The incremental changes in correlation energy due to adding successive functions in an even tempered expansion for a given angular symmetry demonstrate the same tendency toward exponential convergence observed for the first row.

In the correlation consistent basis sets (cc-pVXZ, in general), all of the basis functions that make approximately equal contributions to the correlation energy are added to the basis set at the same time. Therefore, the cc-pVXZ set is improved by adding an entire "shell" of functions to form the cc-pV(X+1)Z set. The first shell of correlation functions for boron through neon and aluminum through argon is (1s1p1d). This shell is added to the atomic Hartree-Fock (HF) orbitals to obtain the cc-pVDZ basis set. The second shell includes an additional (1s1p1d1f) and so on. In practice, the (*sp*) functions are taken from appropriate HF primitive sets. These functions have been shown to differ little from the optimum ones. Thus, as the correlation set is improved, the size of the HF (*sp*) sets is also increased. Therefore, the sets converge upon both the HF and correlated limits. Basis sets of double zeta, triple zeta, quadruple zeta, and quintuple zeta quality have been determined for each of the second row atoms, Al-Ar.

For each of the "standard" sets we have also determined an extended set that has been augmented⁽³⁾ with diffuse functions to better describe electron affinities and other molecular properties (dipole moments, polarizabilities, hydrogen bond energies, etc.). The exponents for the additional *s*- and *p* functions were obtained by optimization for the anion HF+1+2 energy, while the exponents for each of the additional polarization functions were optimized for the anion HF+1+2 energy.

Correlation consistent basis sets systematically approach the complete basis set limit: as basis quality is increased, additional functions provide a progressively better description of both the radial and angular function spaces for *both* the HF and correlated wave functions.

Intrinsic Errors in Correlated Molecular Wave Functions: Configuration Interaction Calculations on First Row AH, A₂, and AB Molecules

The description of fundamental molecular processes using computational electronic structure techniques often requires a sophisticated treatment of electron correlation. However, the resulting accuracy of the molecular wave functions can vary greatly with the size of the one-particle basis set used to represent the molecular orbitals. Often a more accurate correlated electronic structure method is used with a less accurate, one-particle basis set. This leads to erratic results that inhibit our understanding of the true errors associated with the chosen correlated method. The *inherent accuracy* of a correlated electronic structure method can only be assessed if the CBS limit can be determined.

Unfortunately, a regular convergence pattern is usually not obtained upon extending the basis sets in common use today. Thus, it has not been possible to estimate the *intrinsic* errors in correlated molecular wave functions and, hence, in molecular properties such as D_e , r_e , ω_e , etc. Certainly very large basis sets have been developed that have the potential of yielding very accurate results [e.g., the basis sets based on atomic natural orbitals (ANO)].⁽⁴⁾ However, the systematics of these basis sets have not been well explored. In addition, the ANO sets are not the most efficient sets to use in molecular calculations. On the other hand, the correlation consistent basis sets recently developed by Dunning and coworkers⁽¹⁻³⁾ form a family of basis sets that are compact, converge to the CBS limit, and are well defined with respect to increases in size and accuracy. By using systematically larger correlation consistent basis sets, it has been found that many molecular properties converge smoothly to an asymptotic limit that appears to correspond to the CBS limit. By comparing the CBS limits to experimental measurements it is possible to determine the *intrinsic* errors associated with the chosen electronic structure method.

In the present work potential energy functions have been calculated for the electronic ground states of the first row hydrides (BH, CH, NH, OH, HF), homonuclear diatomics (B₂, C₂, N₂, O₂, F₂), and selected heteronuclear diatomics (BO, CN, CO, NO, and OF). The calculations are based on single reference (HF+1+2) and multireference (GVB+1+2 and CASSCF+1+2), internally contracted,⁽⁵⁾ single and double excitation configuration interaction wave functions. The convergence of the derived spectroscopic

constants, dissociation energies, and dipole moment vibrational matrix elements with respect to systematic increases in the size of the one-particle basis set has been investigated for each method. Using sets of double (cc-pVDZ) through quintuple (cc-pV5Z) zeta quality, the CBS limits for D_e , r_e , and ω_e have been estimated for each of the above methods. The effect of adding extra diffuse functions to the basis set has also been addressed using augmented correlation consistent basis sets (aug-cc-pVXZ).⁽³⁾ Finally, the contraction errors associated with the internally contracted multireference CI have been determined for the AH and A₂ species. These errors are found to increase with the number of electrons, but they are, in general, small for all calculated spectroscopic constants.

Figure 1.1 shows the basis set convergence behavior for the calculated CAS+1+2 values of D_e for the A₂ species. As has also been found for the AH species, these results are well fit by functions of the form

$$D_e = D_0 e^\infty + B e^{-CX}$$

where $D_0 e^\infty$ is an estimate of the CBS limit. The calculated intrinsic errors in D_e for the CAS+1+2

Figure 1.1. Calculated CAS+1+2 equilibrium dissociation energies (kcal/mol) using the cc-pVXZ basis sets (■) and aug-cc-pVXZ basis sets (●) for the first row homonuclear diatomics are compared to the experimental values (solid horizontal line). The solid lines are exponential fits through the calculated points.

method are depicted in Figure 1.2 for all the AH and A_2 species, where the differences between the derived CBS limits and experimental results are plotted. Nearly monotonic behavior is observed with errors ranging from < 0.5 kcal/mol for BH and B_2 to ~ 3.8 kcal/mol for F_2 .

The basis set convergence of selected one-electron molecular properties has also been investigated for the AH and AB species. Figures 1.3 and 1.4 show the convergence of the vibrational matrix elements of the (CAS+1+2) dipole moment, $\langle 0|\mu|0\rangle$ and $\langle 0|\mu|1\rangle$, respectively, for OH and CO. Especially interesting is the effect of adding diffuse functions to the basis set; this appears to lead to significantly faster convergence, particularly for the $v = 0-1$ matrix elements.

Modeling Molecular Processes in Clusters

Cluster chemistry plays an important role in the Molecular Theory and Modeling program. The effort is focused on the structure and properties of aqueous clusters and the energetics and dynamics of molecular processes involving such clusters. This work will greatly enhance our understanding of the intermolecular interactions between solutes and water and will provide detailed insights into the "local" effects of solvation on chemical reactions.

Figure 1.2. The intrinsic errors in D_e from the CAS+1+2 calculations for both AH and A_2 species. The intrinsic error is defined as the difference between the estimated CBS dissociation energies D_0^∞ obtained from exponential fits to the calculated CAS+1+2 values and experimental results.

Figure 1.3. CAS+1+2 ground vibrational state dipole moments for OH and CO using the using cc-pVXZ basis sets (■) and the aug-cc-pVXZ ones (●) are compared to experimental results (solid horizontal line).

Modeling Water Clusters, $(H_2O)_n$, $n=1-3$

To accurately describe water-water and ion-water interactions the dipole moment and polarizability of water must be accurately described. We have examined the dipole moment and polarizability for a single water molecule using HF, MP2, and MP4 methods with the new correlation-consistent basis sets.^(1,2,3) Both quantities show a smooth convergence towards a well defined limit. Furthermore, the results obtained at the MP2 level with the aug-cc-pVDZ basis set are within 1% of the experimental dipole moment and within 3.5% of the experimental polarizability. The optimal geometry of the water molecule at this level of theory predicts an HOH angle (ϕ_{HOH}) of 103.8° and OH bond lengths (R_{OH}) of $0.965 \text{ \AA}$; the experimental values are 104.5° and $0.957 \text{ \AA}$, respectively.

The ability of the correlation-consistent basis sets to accurately describe the binding between two water molecules at the MP2 level has been recently demonstrated.⁽⁶⁾ It was found that agreement with the

Figure 1.4. Calculated CAS+1+2 $\nu=0-\nu=1$ dipole moment vibrational matrix elements for OH and CO using the cc-pVXZ basis sets (■) and the aug-cc-pVXZ ones (●).

experimental binding energy⁽⁷⁾ of 5.4 ± 0.7 kcal/mol is excellent even with the smallest of the augmented sets (aug-cc-pVDZ). Expansion of the basis set has little effect on the binding energy: 5.17 (aug-cc-pVDZ), 5.10 (aug-cc-pVTZ), and 5.05 (aug-cc-pVQZ) kcal/mol (without corrections for basis set superposition error). The optimal geometry of the water dimer obtained with MP2 and the aug-cc-pVDZ basis set is shown in Figure 1.5. The harmonic vibrational frequencies for the water dimer have also been computed and compared with results from previous calculations as well as with experimental data. It is important to note that inclusion of diffuse functions in the basis set is essential to achieving an accurate description of the water-water interaction (e.g., the cc-pVDZ basis set predicts a binding energy of -7.5 kcal/mol).

For the water trimer (see Figure 1.6), we also find that the hydrogen bonds between the three water molecules are nonlinear with deviations from linearity of 28.9° , 31.6° , and 28.7° for $\phi_{O_1HO_2}$, $\phi_{O_2HO_3}$, and

Figure 1.5. Geometrical parameters defining the structure of the water dimer.

Figure 1.6. Optimal structure of the water trimer.

$\phi_{O_3HO_1}$, respectively, compared to the experimentally estimated values⁽⁹⁾ of 28° , 30° , and 27° , respectively. We compute a value of $0.978 \text{ \AA}$ for the OH bonds that are part of the ring and $0.964 \text{ \AA}$ for those that do not participate in hydrogen bonds. Finally the binding energy of the trimer is estimated to be -11.2 kcal/mol including zero-point energy corrections.

All calculations⁽⁹⁾ reported in this study were performed with the GAMESS,⁽¹⁰⁾ HONDO,⁽¹¹⁾ MOLPRO-92,⁽¹²⁾ and Gaussian-90⁽¹³⁾ suites of programs.

Modeling Anion-Water Clusters: $F^-(H_2O)_n$, $n=1-3$

In our continuing studies of anion-water clusters, we have computed the optimal structures, harmonic vibrational frequencies and relative energetics of the $F^-(H_2O)_n$, $n=1-3$ clusters at the MP2/aug-cc-pVDZ level. This level of theory not only provides a reasonable description of the water molecule and the structure and bonding of small water clusters, but also of the electron affinity of fluorine (3.54 eV versus the experimental value of 3.40 eV). The optimal structures of the clusters of fluorine anion with one, two, and three water molecules are shown in Figure 1.7. We observe the same structural pattern found for the water clusters of the hydride ion:⁽¹⁴⁾ they exhibit asymmetric structures with the water molecules clustering on one side of the ion. For the $n=2$ cluster the two water molecules are bonded via different F-H bond lengths, although the difference is significantly less than in $H^-(H_2O)_2$, and they form a weak hydrogen bond: the O-O separation is 3.22 Å, as opposed to 2.91 Å for the water dimer, and the OHO angle to 2.91 Å for the water dimer, and the OHO angle

deviates from linearity by 72°. The structure of the $n=3$ cluster has C_3 symmetry with all three water molecules clustering on the same side of the ion. The computed energetics for the successive addition of water molecules to the fluorine ion are compared with the experimental results⁽¹⁵⁾ in Figure 1.7.

Modeling Molecular Processes in Solution

Solution-phase chemistry plays a central role in the Molecular Theory and Modeling program. The effort is focused on the structure and energetics of aqueous clusters and the energetics and dynamics of molecular processes in aqueous solutions. This work is the basis for an enhanced understanding of molecular processes occurring in contaminated groundwater and complex waste solutions. This core program in solution chemistry is designed to further the understanding of the fundamental molecular processes occurring in solution (e.g., solvation and reaction), providing a basis for the development of accurate techniques for simulating the behavior of complex waste solutions.

Modeling the Effect of Solvent Polarization on Solute Structure: The Dipole Moment of Water Molecules in Bulk Water

Molecular processes occurring in the condensed phase can differ significantly from their gas phase counterparts when collective solvent structure creates electrostatic fields that strongly interact with the solute system. These fields can significantly alter properties of a solute such as its energy and electronic structure. Approaches that treat each solvent molecule on the same level as the solute system, such as those that explicitly determine the electronic structure of each individual solvent molecule, are not only intractable but are often unnecessary in the case where the collective classical long-range electrostatic nature of the solute-solvent and solvent-solvent interaction dominates. In this case, emphasis can be placed on determining the electronic structure of the solute (using previously discussed techniques). At the other extreme, a popular technique is to ignore all molecular properties of the solvent and represent the solvent as a uniform continuum dielectric and place the solute inside a spherical cavity inside the dielectric.⁽¹⁶⁾ Although a qualitative understanding of the properties of the solute system may be obtained from such an approach, due to the sensitive dependence of the shape and size of the cavity, quantitative results are dependent on the nature of its parametrization. In

Figure 1.7. Optimal geometries and relative energetics of the $F^-(H_2O)_n$, $n=1-3$ clusters.

addition, it is also necessary to determine the energetics associated with forming the cavity itself.

In this work we consider a simple solute and a well characterized solvent to be used as a critical test for approaches to treat more complicated systems. For our solute we consider a single water molecule and concentrate on electrostatic properties such as its dipole and quadrupole moment and geometric properties such as its equilibrium bond length and angle. For our solvent, we take a homogeneous bath of water molecules in thermal equilibrium with the chosen solute water molecule. For this system the collective geometric structure of water can be accurately obtained from molecular dynamics simulation using an empirical TIP4P water potential.⁽¹⁷⁾ Radial distribution functions obtained from simulations using this potential reproduce those obtained from neutron diffraction measurements. For the properties of the solute, electronic structure calculations at an HF level of theory with a moderately sized basis set can efficiently obtain geometric and electrostatic properties. The essential step of this work is the self consistent manner in which information obtained from electronic structure calculations are combined with information obtained from molecular dynamic simulations.

The procedure we use is as follows. We start by collecting an ensemble of characteristic solvent configurations. This is obtained from a 10-picosecond ($\text{ps} = 10^{-12} \text{ s}$) molecular dynamics simulation of 108 TIP4P waters, rethermalizing the system every 0.1 ps so that the configurations correspond to a canonical ensemble at 300 K. We save the resulting configuration after every 1 psec to obtain 10 "snapshots" of the system. Since our solute is the same molecule as our solvent, the solvent structure of the remaining 107 water molecules around a chosen water molecule represents a characteristic solvent structure. From the 10 snapshots of the system, we consider a complete ensemble of 1080 configurations. For each of the 1080 configurations, we perform an electronic structure calculation at the HF level of the central water molecule in the presence of the collective electrostatic charge density of the remaining waters using an aug-cc-pVDZ basis set.⁽³⁾ We represent the electrostatic interaction from the solvent by including the TIP4P point charges of the solvent molecules in the electronic structure calculation. From the ensemble of 1080 electronic structure calculations we obtain an equilibrium distribution of the resulting properties. In Figure 1.8 we display the

Figure 1.8. Calculated thermal distribution of water dipole moments in bulk water at 300K. The experimental gas phase value is noted on the figure.

resulting distribution of dipole moments. The mean of this distribution is at 2.6 D, which is consistent with estimates of the dipole moment of a water molecule in ice and values obtained from the unfolding of spectroscopic data.⁽¹⁸⁾ The standard deviation of the distribution is about 0.3 D. The whole distribution has shifted from the computed gas phase value of 1.96 D (HF with the aug-cc-pVDZ basis set; the accepted gas phase value is 1.85 D).

Using an Onsager cavity model, it is possible to find a value for the cavity radius that reproduces the mean value. (See Figure 1.9.) Unfortunately, information about the spread of the dipole moment cannot be easily obtained from such a model. To do so it would be necessary to consider statistical fluctuations of the cavity and dielectric constant. Note that the mean value is recovered with a cavity radius of $3.1 a_0$ while fluctuations set the range from about 2.8 to $5.0 a_0$. From the resulting ensemble of solvent configurations it is possible to determine the average polarization structure around the solute. The resulting structure is far from being uniform, and far from being spherical. The first solvation shell structure is clearly visible as well as the influence of average rotational and librational motion of the first solvent shell.

Figure 1.9. Dipole moment of water calculated by HF/aug-cc-pVDZ in a cavity immersed in a homogeneous dielectric with $\epsilon = 80$.

Development of Nonadditive Intermolecular Potentials for Water

Modeling of solutes in aqueous solutions requires accurate water-water interaction potentials as well as solute-water interactions. This is especially true for ionic solutions where polarization of the water molecules by the ions can strongly affect the water-water interactions. The goal of the present work is the development of an improved version of a nonadditive intermolecular model for water that explicitly includes the nonadditive polarization energy. The improved model⁽¹⁹⁾ is based upon the POL1 model developed by Caldwell, Dang, and Kollman.⁽²⁰⁾ To improve the POL1 model, a new set of atomic polarizabilities is developed that reproduce the experimental molecular polarizability for water using the atom-dipole interaction model.⁽²¹⁾ Using the new atomic polarizabilities, the Lennard-Jones parameters are optimized for O-O interactions to fit a range of experimental data.

The thermodynamic results and radial distribution function obtained from molecular dynamics simulations with the improved and POL1 models are compared with corresponding experimental data in Table 1.1 and Figure 1.10. As expected, the improved

Table 1.1. Molecular-dynamics simulation results for various water models.

	Improved Pot'l	POL1 ^(a)	Exp. ^(b)
ρ (g cm ⁻³)	0.994	1.003	0.995
U (kcal/mol)	-9.94	-9.84	-9.92
U_{pol} (kcal/mol)	-2.96	-2.48	
U_{dimer} (kcal/mol)	-5.5	-5.5	-5.4±0.7
r_{dimer} (Å)	2.82	2.80	2.94
α_{water} (Å ³)	1.47	0.99	1.47
μ_{total} (D)	2.62	2.51	~2.60 ^(c)

(a) Reference 20.

(b) Reference 22 (unless specified otherwise).

(c) Reference 18.

Figure 1.10. Oxygen-oxygen radial distribution functions: The dotted line represents the POL1 results, the dashed line is for the X-ray results and solid line is for the results of the improved model.

model provides better results for the properties of water than POL1. For instance, the liquid density and the average potential obtained from the improved model agree well with experimental measurements. The average dipole moment of 2.62 D from the model agrees well with the value of 2.6 D estimated by Coulson and Eisenberg⁽¹⁸⁾ and the work of

Schenter (see previous abstract). In addition, the calculated O-O radial distribution function (RDF) of this model has improved over the O-O RDF of the POL1 model.

Solvation of Cl⁻: A Comparison of Additive and Nonadditive Intermolecular Potentials

An accurate description of ionic interactions in clusters and in solutions is of fundamental importance to the chemical physics of solvation. Recently it has been recognized that nonadditive effects must be taken into account to correctly describe the properties of ionic clusters and ionic solutions. In this section, a systematic study of the importance of nonadditive effects is described.

Molecular dynamics techniques are used in an extensive study on the effects of nonadditive interactions on the solvation properties for a Cl⁻ ion in clusters and in solutions. The water-water intermolecular potential is a polarizable model that we recently developed to explicitly include the nonadditive polarization energy.⁽¹⁹⁾ We developed ion-water additive and non-additive intermolecular potentials in a mutually consistent way; thus, our demonstration of nonadditive effects is more rigorous than those reported in previous works.⁽²³⁾ We calculated the successive H₂O binding energies and structural properties of Cl⁻(H₂O)_n (n=1-7) clusters including simulations of aqueous ionic solutions. From these studies, we concluded that the simulations employing additive potentials overestimated the enthalpies of binding and the hydration number. In contrast, the simulations that employ nonadditive potentials consistently provide good predictions of the enthalpies of binding,⁽²⁴⁾ the solvation enthalpy,⁽²⁵⁾ and the hydration number.⁽²⁵⁾ These results are summarized in Tables 1.2 and 1.3.

Molecular Dynamics Simulations of Fluoride-Fluoride Association in Water

An accurate determination of the interionic potential of mean force (PMF) or solvent-averaged force of an ion pair in water by either computer simulation or theoretical techniques remains a central problem in the chemical physics of solvation.⁽²⁶⁾ For example, the PMFs for an F⁻-F⁻ ion pair in water or a water-like solvent have been calculated using integral equation techniques.⁽²⁷⁾ These calculations indicated strong attractions between the ions near contact. Friedman et al.⁽²⁸⁾ computed the distinct diffusion coefficients for the F⁻-F⁻ ion pair in water and

Table 1.2. Calculated and experimental enthalpies of binding (kcal/mol) of Cl⁻-(H₂O)_n at 300 K.

n	Additive potential	Nonadditive potential	Exp. ^(a)
1	-14.6±0.5	-14.6±0.5	-14.7
2	-28.3±0.8	-27.7±1.0	-27.7
3	-41.9±1.0	-40.5±1.3	-39.5
4	-54.5±1.4	-51.4±1.6	-50.1
5	-66.6±1.7	-61.9±1.8	-59.6
6	-78.0±1.9	-71.0±2.0	-68.4
7	-89.0±2.2	-80.2±2.2	-76.5

(a) Reference 24.

Table 1.3. Averaged solvation properties (kcal/mol) and structural properties for the Cl⁻ anion at 300 K.

	Additive Pot ¹	Nonadd. Pot ¹	Exp. ^(a)
R _{IO} (Å)	3.1	3.2	3.1-3.3
R _{IH} (Å)	2.2	2.2	2.2-2.3
Coordination			
number	6.9	6.3	6.0
ΔH _{sol} (kcal/mole)	-86	-82	-82

(a) Reference 25.

compared the results with experimental measurements. They suggested that the PMF with a strong attraction near contact gave incorrect distinct diffusion coefficients. On the other hand, experimental evidence from NMR relaxation studies by Hertz et al.⁽²⁸⁾ on the association of the F⁻-F⁻ ion pair in water was inconclusive. Thus, at present, it appears that a reliable PMF, including the related thermodynamic properties for an F⁻-F⁻ ion pair in water, has not yet been established. We feel it is important to compute the PMF using a different approach, such as a computer simulation technique.

The PMF for an F⁻-F⁻ ion pair at room temperature was calculated using a rigid simple point charge (SPC/E) water model and molecular dynamics techniques. The results of this simulation are shown in Figure 1.11. The PMF displayed a minimum at an ion-ion separation of 4.3 Å with a barrier height of approximately 1.5 kcal/mol. The barrier height is a

Figure 1.11. The PMFs for the ion pair in water of a molecular dynamics simulation using an Ewald summation technique.

result, in part, of the presence of two water molecules that simultaneously hydrogen bond to both fluoride ions. To investigate the effect of the ionic charge on the hydration properties of an ion pair, we also computed the PMF for the F^+-F^+ ion pair. Our calculations indicated that the barrier height of this PMF is less significant than the corresponding barrier height observed in the computed PMF of the F^--F^- ion pair. This result is reasonable because of the absence of the highly favorable hydrogen bonding between water molecules and the ion pair. When comparing the results of these calculations with those reported in previous works on similar systems using integral equation techniques, our simulated F^--F^- PMF displays more structure and the minimum well depth is shallower; however, the barrier to dissociation is comparable.

Temperature Dependence of the Interactions of a Sodium-Chloride Ion Pair in Water: A Molecular Dynamics Study

We report a comparative study of the PMF and the related thermodynamic properties for a Na^+-Cl^- ion pair using an SPC/E water model⁽²⁹⁾ at two different

temperatures, 298 K and 373 K. Understanding the interactions of ion pairs in solution at high temperature is important in geochemistry and corrosion problems. The PMFs were calculated using thermodynamic perturbation theory⁽³⁰⁾ and the long-range interactions were evaluated using an Ewald summation technique.⁽³¹⁾ The results of the work are shown in Figure 1.12. The PMFs for both temperatures display two minima corresponding to the contact and solvent-separated ion pairs; however, they are different in details. At room temperature, the solvent separated region is favored over the contact region. In contrast, the calculated PMF at higher temperature indicates that the contact ion pair is more favorable. These observations are in general agreement with a recent Raman study of salt solutions of similar systems.⁽³²⁾

Our calculated PMF at room temperature is very similar to one previously calculated using a flexible water model.⁽³³⁾ This result suggests that the more stable solvent-separated ion pair at room temperature may not be due to the inclusion of the internal motions of water molecules. It is probably due to the balancing of the intermolecular forces.

Figure 1.12. The PMFs for the Na^+-Cl^- ion pair in water at 298 and 373 K using an Ewald summation technique.

Critical Comparison of Approximate and Accurate Quantum Mechanical Calculations of Rate Constants for a Model Activated Reaction in Solution

Benchmark quantum scattering calculations of rate constants for gas-phase chemical reactions have played an important role in establishing the validity of approximate methods that can be applied to a wider range of more complex problems. Although benchmark quantum mechanical calculations of rates of activated reactions in solution would be invaluable for testing approximate methods being developed for these systems, none have appeared in the literature. In this work, accurate quantum mechanical calculations of rate constants for a model of a reaction in solution are used as benchmarks for two approximate methods: 1) improved canonical variational theory (ICVT) with the small curvature semiclassical adiabatic ground-state (SCSAG) correction for reaction coordinate motion,⁽³⁴⁾ and 2) the path integral centroid density method.⁽³⁵⁾ The reaction model corresponds to a single solute coordinate that is linearly coupled to a collection of harmonic oscillators. This model has been shown to be equivalent to a generalized Langevin equation (GLE) for the solute coordinate and has been the subject of numerous studies of the influence of dissipative medium of quantum mechanical tunneling.

In this work we consider the special case of a single-oscillator solvent. This model can be treated by accurate quantum mechanical methods. The potential for the solute coordinate is taken as an Eckart potential that is parametrized to mimic the $\text{H} + \text{H}_2$ reaction. The bath parameters (the harmonic bath frequency and coupling constant) are obtained by fitting them to a Gaussian friction kernel that would be used in the GLE. Calculated reactive fluxes (the product of the thermal rate constant and reactant partition function) are reported as functions of the bath parameters which are characterized by the time scale of the friction kernel (slow, medium, and fast) and a unitless measure of the strength f .

Critical comparisons of reactive fluxes computed with the approximate methods (centroid density method and ICVT/SCSAG) with those from accurate quantum mechanical calculations on the reaction model indicate that the approximate methods provide reliable estimates of quantum tunneling effects in regions where they are important. It is interesting to note that for all three frequencies of the bath oscillator (slow, medium, and fast time scales of the friction) at both 200 and 300 K, the approximate methods give

excellent agreement with the accurate quantum mechanical calculations for very low values of the friction near $f=0$ and as the friction becomes very large. In the zero-friction case, the problem reduces to one-dimensional tunneling, and both approximate methods handle this case very well. At very large values of the friction, the harmonic part of the Hamiltonian dominates, motion along a reaction coordinate requires moving the bath oscillator coordinate, and tunneling is greatly diminished. In these cases, the approximate methods once again handle the harmonically dominated problem very well. It is the intermediate friction region where tunneling in the multidimensional system is most important and provides the most severe test of the approximate methods.

For the systems with the largest harmonic frequency of the bath oscillator (the fast friction), both of the approximate methods gave excellent agreement with the accurate quantum mechanical results. The agreement was not as good for the systems with lower frequency for the bath oscillator (the medium and slow values of the friction) and at intermediate friction strengths. Results are shown in Figure 1.13 for the

Figure 1.13. Reactive flux at 300 K as a function of reduced friction for the Eckart potential linearly coupled to a single harmonic oscillator. Results for accurate quantum flux correlation function calculations ($\bullet$), ICVT with SCSAG tunneling correction (Δ), and path-integral centroid density method ($\square$) are shown for the slow time scale friction.

case of the slow friction at 300 K. The agreement was still semiquantitative with the largest error being a factor of 2.1 overestimate for the centroid density method and a 42% underestimate for the ICVT/SCSAG method when anharmonic effects are included in the calculations. Presumably, the centroid density results could be improved in this case by moving the dividing surface for the path centroid constraint. Such a variational centroid density method is discussed below.

Quantum Mechanical Rate Theories: Centroid-Density Path-Integral Approaches

Transition state theory (TST)⁽³⁶⁾ is the simplest method for calculating rate constants for multidimensional systems since its expression for the rate constant involves the evaluation of thermodynamic equilibrium averages and no explicit dynamics are required. Classically, TST gives an upper bound to the exact rate constant and the lowest upper bound can be found by variationally optimizing the transition state dividing surface. For reactions such as proton or hydride transfer, quantum mechanical effects are important and generalizations of variational transition state theory (VTST) to include these effects have been highly successful. For example the ICVT/SCSAG method quantizes the bound degrees of freedom and includes multidimensional transmission coefficients to account for tunneling in the reaction coordinate motion.⁽³⁴⁾

An alternate method for including quantum mechanical effects into a TST framework is the centroid-density path integral rate theory.^(35,37) In this approach quantum mechanical effects for the bound degrees of freedom and reaction coordinate are included by an approximate path integral expression that constrains the centroid of the quantum paths to be located on the dividing surface. Previous applications of this theory have placed the dividing surface at the saddle point and characterized it by a single coordinate. In this work we seek to combine the numerical tractability of imaginary time Feynman path integrals for calculating multidimensional partition functions with the conceptual foundation of variational transition state theory.

We have developed a method that is based on centroid constrained Feynman path integration, thus allowing for arbitrary dividing surfaces. This is achieved by recasting the rate constant in terms of phase-space path integration. The resulting expression for the microscopic rate constant takes the form

of the classical rate expression—an equilibrium average of the product of the flux through the dividing surface and the projector of states that lead to reaction. In the quantum expression, the classical Boltzmann distribution function is replaced by a centroid-constrained phase-space path integral expression for the density function. The dynamical factor associated with the projection of states leading to reactive motion is put on the same footing as the evaluation of the flux through the dividing surface. This allows arbitrary definitions of the dividing surface. The transition state theory approximation to this dynamical factor projects all phase-space points that have flux through the dividing surface headed in the product direction. In this case the high temperature recovers the classical variational TST result. For a harmonic system, the variationally obtained rate from our method recovers the exact rate. We can further improve our method by using classical mechanics to estimate the projector of reactive motion. In this “dynamical centroid approach,” the exact expression for the rate is recovered in the classical limit.

To test the methods we compare our results to the previously discussed accurate quantum mechanical calculations on the model of an Eckart potential coupled to a single harmonic oscillator. In Figure 1.14 we show the systematic improvement of the results with the increased sophistication of the method. By allowing the dividing surface to move away from the saddle point, the variational centroid results recover the high coupling results. By using classical mechanics to recover classical recrossing effects, the dynamical centroid recovers the low coupling results.

Inclusion of Solvent Continuum Effects in Variational Transition State Theory

The constant proximity of solvent molecules can alter the interaction energies between solute molecules and their dynamics through both localized and collective interactions. Localized effects can be reliably treated by clusters. However, certain long-range (collective) effects will not be adequately handled by the size of clusters that can currently be conveniently studied. In these cases, the collective effects can often be included using approximate methods. For example, solvent polarization effects on interaction energies and other properties of the solute can be included in a continuum dielectric model. Calculations of solvent polarization effects on reaction energetics using a continuum dielectric model assumes that the solvent polarization adjusts instantaneously to changes in

Figure 1.14. Reactive flux at 300 K as a function of reduced friction for the Eckart potential linearly coupled to a single harmonic oscillator. Results for three versions of the centroid density path integral method – nonvariational (—), variational (○), dynamical (□) – and accurate quantum flux correlation function calculations (●) are shown for slow friction.

the solute. For orientational polarization effects that correspond to reorientation of dipoles in a polar solvent, the time scale for the rotational motion of the dipoles is often similar to the times scale of motion in the solute. In this case, the solvent polarization may not be in equilibrium with the field arising from the solute charge density.

The effect of nonequilibrium solvent polarization on chemical reactions was first treated by Marcus⁽³⁸⁾ in his landmark treatment of charge transfer in solution. Lee and Hynes⁽³⁹⁾ have shown how to introduce a generalized microscopic coordinate representing macroscopic solvation (in terms of orientational polarization) and how this can be used within a dynamical theory to include the effects of nonequilibrium solvation on charge transfer reactions in polar solvents. Although the model is restrictive in its treatment of the orientational polarization, it provides an example of how the influence of a multi-dimensional solvent can be treated with only a small number of effective solvent coordinates. They have combined the solvent coordinate model with VTST^(34,40) to treat several examples in model studies.⁽⁴¹⁾

The goal of the present study is to generalize the Lee-Hynes formalism to allow more systematic treatments of arbitrary reactions. In the Lee-Hynes formalism, a single effective solvent coordinate is defined in terms of changes of the reorganizational polarization of the dielectric media that is modeled in terms of variations of charges ϵ_a on the atoms (or moieties) α as a function of a single solute reaction coordinate s . This approach will not model reactions involving motion of charges through the dielectric media with little or no changes in the atomic charges themselves. As an example, S_N1 reactions in regions of large interionic separations will involve little or no variation in charges, but the reorganizational polarization of the dielectric media will change because of relative movement of the charges. Furthermore, internal motion of the solute other than just the reaction coordinate motion can also cause changes in the reorganizational polarization that can couple to the reaction coordinate motion and affect the reaction rate. Therefore, in this work we have extended the formalism by 1) modeling changes of the reorganizational polarization in terms of variations of internuclear separations of the charges as well as changes in the charges themselves, 2) representing variations of the internuclear separations and charges using other internal motions of the solute in addition to the solute reaction coordinate, and 3) removing the restrictive interpolation model for the solute charges used previously. The internal modes of the solute are conveniently defined in terms of generalized transition-state cartesian coordinates.⁽⁴⁰⁾ In this formalism, VTST calculations are complicated by coordinate dependence of the solvent masses. To treat this, we define a canonical transformation to coordinates that do not contain this dependence based upon geodesic and parallel transport equations.

Application was made to a simplified model S_N2 reaction that incorporates a single solute reaction coordinate and a single solvent coordinate. The solute coordinates were modeled by an Eckart potential using three sets of parameters. Solute I fits the barrier height and barrier frequency to model the symmetric $\text{Cl}^- + \text{CH}_3\text{Cl}$ reaction in water. The other two sets of parameters, Solute II and Solute III, are asymmetric potentials with the same frequency and barrier heights, and energy differences between reactants and products that are 90% and 99% of the barrier height, respectively. The solvent polarization was modeled by an extension of the Generalized Born fragment model,⁽⁴²⁾ and the nonequilibrium polarization was modeled by the changes in the charges (as a

function of the solute coordinate) by a Maclaurin series about the saddle point. Two sets of parameters for the Maclaurin series were taken from a fit to *ab initio* data and from the model of Lee and Hynes.⁽⁴¹⁾ For the six models of an S_N2 reaction, we have calculated classical rate constants by conventional transition state theory and canonical variational theory for equilibrium and nonequilibrium solvation.

The results in Table 1.4 show that the effect of nonequilibrium solvation can be appreciable. For Solvent Model I, the change in charge near the saddle point is sufficiently small that coupling between the solute and solvent coordinates is small in the region of the saddle point. For Solute Models I and II, the intrinsic barrier is sufficiently high that the optimum location of the transition state remains at the saddle point. However, for Solute Model III, the small intrinsic barrier, 0.3 kcal/mol, allows the variational dividing surface to be moved to a region of the potential where coupling between the solute and solvent is stronger and, for this model, nonequilibrium solvation effects are greatly enhanced. Solvent Model II has larger changes in charge near the saddle point and, as a result, coupling between the solute and solvent is larger and nonequilibrium solvation effects are also larger. For this model of the solvent, the intrinsic barrier does not have to be nearly as small (compared to Solvent Model I) before the effect of variationally optimizing the dividing surface is important.

Table 1.4. Ratios of nonequilibrium solvation to equilibrium solvation rate constants using conventional transition state theory ($\ddagger$) and canonical variational theory (CVT) at 298 K.

Solute Model	Solvent Model	$\ddagger$	CVT
I	I	0.96	0.96
II	I	0.96	0.96
III	I	0.96	0.25
I	II	0.69	0.69
II	II	0.69	0.18
III	II	0.69	0.16

Modeling Molecular Processes in Separations Chemistry

Research in separations chemistry focuses on the structure and energetics of ion-ligand complexes (such as crown ethers) and the dynamics of complex formation in aqueous solutions. The goal of this effort is to discover the factors that control the selectivity and efficiency of ligating species important in the pretreatment of nuclear and chemical wastes. To date the effort has concentrated on *ab initio* calculations of interaction energies including important relativistic effects for heavy elements. In the future, this work will expand to study the dynamics of ligand/ion interactions in aqueous solutions.

Ab Initio Electronic Structure Studies of Molecules and Clusters Using Relativistic Core Potentials

Relativistic effects must be explicitly taken into account in *ab initio* electronic structure calculations on molecular systems involving heavy elements such as Cs and Sr that are important for separations chemistry. These calculations require

1. the use of relativistic effective core potentials (REP) and core-valence polarization potentials (CVPP) to handle the large number of inert core electrons and to include the effect of the relativistic mass-velocity and Darwin terms
2. the explicit inclusion of relativistic (spin-orbit) effects involving the valence electrons.

REPs were derived using *ab initio* numerical Dirac-Fock atomic wave functions and shape-consistent pseudo-spinors. CVPPs were obtained using the adiabatic field method in the context of ω - ω coupled molecular wave functions. REPs and CVPPs were derived for elements having a small number of valence electrons (Li, Be, Cs, Ba) and for the lanthanide elements.⁽⁴³⁾ Valence electrons in molecules and clusters are addressed using a configuration interaction (CI) procedure that incorporates spin-orbit operators extracted from the respective REPs.

The REPs and CVPPs were incorporated in full spin-orbit CI calculations. Prototypical systems such as Cs_2^+ , Cs_2 , and $LiBe$ were treated using this method. In all cases, the inclusion of core-valence polarization potentials raises the energy of each ground state to a value in close agreement with experimental results. The spectroscopic constants and electronic spectra of both valence and Rydberg states of the weakly bound metal dimer $LiBe$,⁽⁴⁴⁾ treated as a three-electron

molecule in the present approach, are in agreement with experimental and large scale all electron *ab initio* results. The method was also applied to the adsorption of K on the Ag(100) surface.⁽⁴⁵⁾

Ab initio self-consistent field (SCF) and CI calculations were carried out for the hydrated cesium ion, $\text{Cs}(\text{H}_2\text{O})^+$. Cs was represented as a nine-electron atom whose 46 core electrons were replaced by an REP. The valence basis set of contracted Gaussian-type functions was $[5s4p2d]$ for Cs, $[3s^?p2d]$ for O and $[2s1p]$ for H. The calculated SCF structure of this complex compares favorably with the empirical model developed by L. X. Dang^(a) for molecular dynamics simulations. Both predict a planar complex with the O atom closest to the ion. The SCF and empirical models predict a Cs-O distance of 3.04 and 2.97 Å, respectively. Vibrational-rotational analyses of poly-atomic potential energy surfaces for the complex and water were performed using the SURVIBTM program. Using this information and the CI energy difference, the heat of formation was computed to be 14.3 kcal/mol, in good agreement with the experimental value of 13.7 kcal/mol of Dzidic and Kebarle.⁽⁴⁶⁾

Modeling Interfacial Molecular Processes

Interfacial processes, especially at the water-solid interface, are important in a number of environmental restoration and waste management problems. The program in Interfacial Chemistry focuses on molecular processes at the water-soil mineral interface and the glass-water interface. The first focus area is important in understanding transport of contaminants through the soil, the second provides information on the long-term stability of stored nuclear wastes.

Research in the chemistry of minerals is directed towards understanding the binding of molecules to soil minerals and the dynamics of molecular processes at the interface between minerals and aqueous solutions. This work is important both to the development of reliable models of contaminant transport and transformation in the subsurface as well as to the development of improved techniques for extracting contaminants from soils. An integrated theoretical approach that combines methods from *ab initio* quantum mechanics and classical mechanics is used. This approach involves both the application of existing state-of-the-art methods to the study of

current environmental problems and the refinement and development of new theoretical methods for treating progressively more complex geochemical systems. An objective of this research is to transfer the knowledge gained from these fundamental studies to large-scale subsurface transport models. This is a joint project with A.C. Hess in the Materials Theory and Modeling Group (see Section 2 for additional details).

The chemistry of amorphous materials focuses on the molecular processes occurring at the interface between amorphous materials and aqueous solutions. The goal is to better understand the degradation of materials (such as glasses) that have been proposed as long-term storage media for nuclear wastes and to aid in the development of new, more stable waste forms.

The Interaction of Water with the (001) Surface of Magnesium Oxide

The adsorption and chemical dissociation of water on oxide surfaces are fundamental processes that must be understood before the chemistry at soil surfaces can be modeled in a meaningful way. Several mineral oxides are known to readily hydroxylate when exposed to subsurface aqueous environments. The structural, chemical, and physical properties of water at these mineral interfaces are expected to greatly influence the behavior of subsurface contaminants.

A theoretical study of water adsorption on the surface of a three layer (001) magnesium oxide (periclase) film has been performed using periodic Hartree-Fock (PHF) theory⁽⁴⁷⁾ with density-functional based correlation corrections.⁽⁴⁸⁾ The object of this work was to probe the energetics of chemidissociation and physisorption processes on a clean mineral oxide surface (Figure 1.15). The calculations treated two water molecules per MgO unit cell (one on each side of the film) and in most of the calculations, the size of the unit cell was chosen such that the ratio of water molecules to surface magnesium ions was 1:4. This corresponds to a water-water spacing between molecules in neighboring cells of 5.95Å. Nine different configurations were examined of which three were strongly bound to the surface. The binding energies for the three favorable configurations were 4.1 - 8.9 kcal/mol from PHF calculations and 6.3 - 12.5 kcal/mol when correlation effects were included. When the geometry of a bound water molecule was allowed to relax at the equilibrium water-film distance, the H-O-H angle increased 1-3° from the free molecule value of 105.6° (with a 6-31G* basis on water) while

(a) L. X. Dang, private communication.

Figure 1.15. Absorption of water on a slab of MgO (001).

the O-H bond distance remained unchanged. The six remaining geometries examined did not show significant binding to the surface at a 1:4 coverage. The formation of a fully hydroxylated surface (one hydroxyl group to every surface magnesium ion and one hydrogen atom to every surface oxygen ion) was examined and was found to be energetically unfavorable. The energetic bias against dissociative chemistry on the clean MgO (001) surface, consisting of fully five coordinated ions, is in agreement with previously published UPS,⁽⁴⁹⁾ XPS,⁽⁴⁹⁾ and IR⁽⁵⁰⁾ studies.

This work indicated that hydroxylation of the surface was energetically unfavorable on a defect-free clean MgO (001) surface. Molecular water does, however, readily adsorb on this surface and is expected to influence the further uptake of contaminants by the mineral. Future work will probe the interaction of molecular species with the MgO/H₂O interface and will investigate the effects of periodic surface defects (kinks and steps) on the surface chemistry. Current studies are also examining the behavior of water and molecular contaminants on the surfaces of the clay minerals kaolinite, pyrophyllite, and talc. In addition,

new theoretical methods are being developed that will incorporate the *ab initio* descriptions of these mineral systems into classical simulations of the interfacial dynamics.

Living Poly- α -Methylstyrene Near the Polymerization Line: II. Phase Diagram in Methylcyclohexane

The underlying mechanism for the degradation of glassy materials in contact with aqueous solutions is a polymerization-depolymerization process of the network forming system. Systems that polymerize under equilibrium, such as living polymers, exhibit this phenomena. A living polymer requires the presence of an initiator that activates the monomer. As the temperature is lowered through its polymerization temperature the polymer grows in equilibrium with its monomers. If termination reactions can be avoided, the polymer molecules remain active, allowing them to grow or shrink as the temperature (or concentration of monomer) is raised or lowered.⁽⁵¹⁾ Results for these systems are used to pave the way for the development of simulation methods of polymerization-depolymerization processes in complex network systems.

The liquid-liquid coexistence curve of living poly- α -methylstyrene initiated by *n*-butyllithium in methylcyclohexane has been experimentally determined and compared with the predictions of the mean-field approximation of the dilute $n \rightarrow 0$ vector model of magnetism.⁽⁵²⁾ The coexistence curve, critical polymerization line, and critical point for this system are experimentally determined by fixing the ratio r of the initiator concentration to initial monomer concentration. The theoretical calculations have been carried out under these same conditions.

In Figure 1.16 the experimental results are compared with the calculated results in the $(T/T_p, x_m^*)$ plane, where T_p is the critical polymerization temperature of neat α -methylstyrene and x_m^* is the initial mole fraction of monomer. Previously, phase diagrams corresponding to living polymer systems were calculated in the limit that the equilibrium constant for the polymer initiation reaction approached zero⁽⁵³⁾ (corresponding to the limit of the magnetic field approaching zero in the magnetic analog), or for the case in which the concentration of the initiator species was held constant.⁽⁵⁴⁾ The phase diagram in this limit is shown as the dot-dash line, calculated for a choice of parameters that gives a symmetric

Figure 1.16. Comparison of experimental data and calculated phase diagram. The calculated critical polymerization line is given by the dotted line, the experimentally determined critical polymerization points are given by the open triangles. The calculated coexistence curves are shown for the case of zero field, dot-dash, that meet the critical polymerization line at a tricritical point, and for the case in which the ratio r is held fixed at non-zero field. The latter are two pairs of curves shown by the solid and dashed curves, where the left solid curve has as its corresponding equilibrium phase the right dashed curve and the right solid curve has as its corresponding phase in equilibrium the left dashed curve. The solid branches both have the specified ratio $r = 0.008$. The closed diamond is the calculated critical point. The open circles are the experimentally determined "cloud points" and the closed circle the experimentally determined critical point.

tricritical point near where the experimental critical polymerization line (open triangles) meets the experimentally determined coexistence curve (open circles). The dotted line is the theoretically determined critical polymerization line in the same limit. [A tricritical point is a point at which a first-order phase transition meets a second-order phase transition. Critical polymerization has been identified as a second-order phase transition in which the heat capacity exhibits a singularity.] In this work the phase diagram is calculated for the fixed ratio r corresponding to a non-zero value, albeit a small value, of the equilibrium constant for the polymer initiation reaction.

The resulting phase diagram has the following properties. For a specified value of r , two coexistence curves that intersect at a critical point are determined. On each of these coexistence curves, one branch has the specified value of r (solid line) and the other branch (dashed line) is the phase in true equilibrium at different values of r . In Figure 1.16, the left solid curve is in phase equilibrium with the right dash curve, similarly for the right solid curve and the left dashed curve. The calculated critical point is the filled diamond and the experimentally determined critical point is the filled circle. The experimental points of the coexistence curve are determined by sealing in a tube initiator, monomer, and solvent at the specified value of r and different x_m^* . The temperature is varied until the cloud point is reached (after several hours two phases are observed). This point corresponds to the branch of the calculated curve that has the specified value of r ; therefore, the calculated phase boundary of interest is represented by the two solid curves.

The calculated phase boundary is apparently asymmetric. If the scaling exponents of the two branches are measured over the range $0.000260 < |(T - T_c)/T_c| < 0.000558$, the resulting effective exponents are $\beta = 0.4$ for the left branch and $\beta = 0.6$ for the right branch. [The effective exponent is just the slope obtained from a log-log plot of $|T - T_c|$ versus $|x_s - x_s^c|$.] In the asymptotic limit, the theory does indeed have the classical scaling exponent of $\beta = 0.5$, and can be verified by expanding the free energy around the critical point for fixed r . A nonclassical result (e.g., renormalization group) would lead to an exponent of $\beta = 0.32$. The above result is a classical one, hence one can expect a much flatter phase diagram, thus a better fit of the experimental data, for a nonclassical solution of the dilute $n \rightarrow 0$ vector model of magnetism.

Modeling Molecular Processes in the Atmosphere

Theoretical Estimate of the Enthalpy of Formation of HSO and the Relative Stability of HSO and SOH

The thermochemistry of HSO is of importance because this species is involved in the atmospheric oxidation of HS, one of the chemical processes that leads to acid rain.^(55,56) It has furthermore been suggested^(56,57) that HSO might be involved in a catalytic cycle that depletes ozone according to the scheme:

Unfortunately, the enthalpy of formation of HSO is not well established, so the thermodynamics of reaction (R2) are uncertain. Estimates of $\Delta H_{f,298}^\circ$ (HSO) have ranged from 14.9 kcal/mol⁽⁵⁸⁾ to -1.4 ± 1.9 kcal/mol.⁽⁵⁹⁾ The standard enthalpies of formation (at 0 K) of O_3 and HS are 34.7 ± 0.4 and 32.6 ± 1.2 kcal/mol, respectively.⁽⁶⁰⁾ In order for reaction R2 to be exothermic, the enthalpy of formation of HSO must be less than -2.1 ± 1.6 kcal/mol.

Another problem of interest is the energy difference between HSO and its SOH isomer. All theoretical studies⁽⁶¹⁾ to date predict SOH to be more stable than HSO by 3-10 kcal/mol. In contrast, only HSO has been observed experimentally. However, in the theoretical studies, the difference between the two isomers was found to decrease both upon enlarging the basis set and upon use of a more accurate level of theory. A more thorough theoretical study was clearly warranted.

We have computed the enthalpy of formation of HSO and the HSO-SOH energy difference using the multireference singles and doubles configuration interaction (MRSD-CI) method and the recently developed correlation-consistent polarized valence basis sets.⁽¹⁻³⁾ The MRSD-CI method, based on a complete active space self-consistent field (CASSCF) wavefunction, has been shown to yield results comparable to that obtained from full CI calculations for diatomic and triatomic molecules. The internally contracted method of Werner and Knowles⁽⁵⁾ was used to efficiently and effectively handle the large CI expansions considered here (up to 165 million configuration state functions). The correlation consistent basis sets provide a systematic way of expanding the orbital basis set (see Benchmark Studies). All calculations were performed using the GAMESS⁽¹⁰⁾ and MOLPRO⁽¹²⁾ suites of programs.

The calculated dissociation energies (including zero point energy) $D_0(\text{H-SO})$ are shown in Figure 1.17 for the aug-cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z basis sets. Extrapolating the calculated values of the H-SO dissociation energy to the "complete" basis set limit, we predict $D_0(\text{H-SO}) = 57.0 \pm 0.3$ kcal/mol (see Figure 1.17). The binding energies computed with the CASSCF+1+2 method, even in the "complete" basis

Figure 1.17. Calculated CASSCF+1+2 binding energies (D_0) for H-SO.

set limit, will still be in error. To obtain an estimate of the error in the H-SO bond energy, we compare with corresponding calculations on the H-S molecule. For HS, CASSCF+1+2 calculations (see Benchmark Studies) predict $D_0(\text{H-S}) = 82.3$ kcal/mol (extrapolated to the "complete" basis set limit); the experimental value is 83.5 ± 0.7 kcal/mol.⁽⁶²⁾ Assuming that the error in H-SO is at least as much as that in H-S, we estimate

$$D_0(\text{H-SO}) \approx 58.2 \pm 1.0 \text{ kcal/mol.}$$

The above D_0 leads to an enthalpies of formation (at 0 K) of -6.0 ± 1.3 kcal/mol and -0.6 ± 1.3 kcal/mol for HSO and SOH, respectively. The corresponding values at 298 K are estimated at -6.1 ± 1.3 and -0.7 ± 1.3 kcal/mol for HSO and SOH, respectively. This suggests that reaction R2 is indeed exothermic.

We also computed the energy difference between HSO and SOH, ΔE_0 , which includes zero-point energy corrections. At the MP2 level with the smaller sets, SOH is more stable than HSO; although, in agreement with previous studies, the absolute value of the energy separation decreases with increasing basis set size. The energy differences from the CASSCF+1+2 calculations show a

smooth convergence, predicting HSO to be more stable than SOH by 5.4 kcal/mol at the "complete" basis set limit. This resolves the apparent disagreement between theory and experiment for the stability of HSO versus SOH.

Interfacial Properties of Nitric Acid Monohydrate

Interfacial processes at the gas/solid or liquid/solid boundaries of ice and hydrated crystalline materials play an important role in regulating the chemistry of different terrestrial environments. An example of this is the catalytic destruction of polar stratospheric ozone in the Antarctic, which is proposed to occur on the surfaces of hydrated nitric acid crystals. Theoretical characterization of the bulk and surface properties of crystalline nitric acid monohydrate (NAM, $\text{HNO}_3 \cdot \text{H}_2\text{O}$) was accomplished using periodic Hartree-Fock theory⁽⁶³⁾ (see Section 2). A description of the bulk material was obtained from calculations of the cohesive binding energy, optimized lattice constants, band structure, total and projected density of states, Mulliken population analysis, electrostatic potentials, and elastic constants. The computed intracrystal interactions were consistent with the proposed hydronium/nitrate ionic crystal structure inferred from X-ray structure data. The calculated elastic constants, interlayer electrostatic potential maps, and characterization of the bonding in the crystal indicated that NAM is composed of weakly bound puckered layers aligned parallel to the (100) plane in the crystal. The properties of this surface were studied using a model system that consists of a two-layer slab of NAM formed by cleaving along the $\langle 100 \rangle$ direction in the crystal. A comparison was made between the computed properties of the bulk material and the model (100) NAM surface.

Maps of the electrostatic potential above and within the slab were used to predict favorable sites for physisorption on the (100) surface of NAM crystals. Figure 1.18 shows a contour map of the electrostatic potential of NAM bulk in a plane along the solid line in the schematic diagram. The dashed lines in the figure are negative regions of the potential that are energetically favorable sites for cations. The potential map illustrates the network of hydrogen bonds

Figure 1.18. Electrostatic potentials for NAM

between the nitrate and hydronium ions in the crystal. According to this plot, a positive test charge would seek the region on the ridge between two hydronium ions and near the up-pointing nitrate in the folded layer. Similarly, a negative test charge would seek the region directly above hydronium ions on the ridge. These locations are proposed as likely physisorption sites on the (100) NAM surface. A real atom or molecule will approach these sites until Pauli exclusion and nuclear repulsion forces overwhelm the electrostatic forces. According to this argument, nucleophiles and negative ends of molecular dipoles would prefer the hydronium sites, while electrophiles and positive ends of molecular dipoles will tend to orient over the nitrate sites.

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2. Materials Theory and Modeling

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Materials theory and modeling plays an important role in many environmental restoration and waste management problems. The development of accurate, predictive models of contaminant flow in the groundwater and the design of effective remediation technologies to remove or immobilize contaminants from the subsurface environment depend on understanding subsurface chemical reactions and their molecular-level mechanisms. Unfortunately, little is even known about the microscopic structure of the mineral surfaces on which these reactions occur.⁽¹⁾

Another area of active interest is the chemistry of zeolites, both for their catalytic properties and for their ability to function as ion exchange media. For example, Na Zeolite-A exchanges Na ions for Cs ions. Hydrothermal treatment then collapses the zeolite structure and, in effect, "shrink-wraps" the radionuclide, thus providing a promising new approach for separating and storing high-level wastes.

Finally, a basic problem confronting the characterization and monitoring of contaminated sites is the need for sensitive and selective chemical sensors to detect and characterize the contaminants.⁽²⁾ Thin-film polymers are often used as selective layers in many chemical sensor devices. Unfortunately, little is known about the properties of the polymer films, or their interactions with analytes on a molecular level. One key to the improvement of existing

selective layers and the manufacture of new high-performance sensor devices is the development of a detailed understanding of energetics and mechanisms of analyte-polymer and polymer-polymer interactions. We are currently embarking on such a program in collaboration with experimental scientists in the MSRC Materials and Interfaces group.

Methods for Periodic Calculations on Solids

There is a strong component of research in the Materials Theory and Modeling program focused on understanding the properties of materials using techniques from *ab initio* solid-state quantum chemistry and physics. The scope of the effort includes both the development of new methods, the refinement of existing technologies, and specific applications to environmentally and technologically important materials.

Contributions to the Development of CRYSTAL

One of the computational methods currently being used to study systems of interest is the periodic Hartree-Fock method. This approach provides SCF solutions to the Hartree-Fock-Roothaan equations subject to periodic boundary conditions. Its primary advantage over nonperiodic (molecular) analogs is that it avoids the limitation of treating crystalline systems as finite molecular clusters by exploiting the full crystallographic space group symmetry of the system. The incorporation of translational symmetry into a calculation eliminates "edge" effects associated with truncating finite clusters and enhances the computational feasibility and accuracy by which one can treat a crystalline material. This approach has been fully implemented in the program CRYSTAL developed by Dovesi, Pisani, Saunders, Roetti, and Causa.^(3,4)

Calculations on realistic solid state problems important in the environment stress the resources of the most powerful computers currently available (see next section). One severe problem is the large amount of I/O to disk required in traditional disk-based algorithm. During the past year Drs. V. R. Saunders, N. M. Harrison, and A. C. Hess have implemented "direct SCF" algorithms into the program CRYSTAL, greatly reducing the disk I/O required. This new technology is actively being used to treat systems previously thought to be beyond the scope of existing technology.

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Chemistry and Physics of Minerals

The Structure and Properties of Clay Minerals

The clay minerals are among the most common decomposition products of aluminosilicates and, because of their large surface areas, these materials play a disproportionate role in ion exchange processes and the transport of chemical species in soils. However, the combination of extremely small particle sizes (typically 2-10 μm), and a tendency of the natural materials to exhibit both structural and substitutional disorder, severely complicates precise experimental characterization of the physical and chemical properties of these materials. Structural characteristics typical of these compounds can be seen in Figure 2.1(a), which depicts the crystal structure of the mineral kaolinite. In general, the clays are layered hydrous aluminosilicates that interact with their environment by intercalating species between the "layers" of the material, at external surfaces parallel to the planes containing a single clay "layer" or on the external "edges" of the material.

We have recently completed periodic Hartree-Fock linear combination of atomic orbitals (LCAO) studies of the bulk properties of the clay minerals kaolinite⁽⁶⁾ ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), pyrophyllite ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$), and talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) using STO-3G and modified 6-21G and 6-21G* basis sets. In these studies, such properties as the electrostatic potential, electric fields, charge density distribution, and density of states were computed, and the positions of the hydrogen lying in the interior of the clay layers were determined. It is important to note that these materials are of extremely low symmetry (space groups P1 or P-1) and frequently contain 20 to 40 heavy atoms per unit cell. As a consequence, *ab initio* calculations using the above described methods severely burden the most powerful computers available today.

In order to investigate the chemical behavior of the external surfaces of kaolinite, we have also carried out analogous calculations on an infinite two-dimensional slab consisting of a single kaolinite layer (one layer of the crystal structure shown in Figure 2.1(a)). All calculations were performed using a 6-21G* basis. It has long been thought that the silicate ring system, the bottom portion of the structure shown in Figure 2.1(b), is one of the most chemically active regions of the mineral's surface.⁽⁶⁾ This region of the structure is composed of corner sharing SiO_4 tetrahedral, three of which link together to form six membered rings. The center of the resulting ring is known

Figure 2.1. Crystal structure of kaolinite. (a) Side view of the kaolinite layers. (b) Top view of the silicate ring system.

as the ditrigonal cavity and has been proposed⁽⁶⁾ to behave as a weak Lewis base due to nonbonding electron density on the ring oxygen atoms.

In order to investigate these assertions, we have determined the spatial behavior of the electrostatic potential from the kaolinite slab calculations. The resulting potential isosurfaces are shown in Figure 2.2. The white colored isosurfaces shown in Figure 2.2 encapsulate the most negative region of the electrostatic potential in the vicinity of the ring. The region can be interpreted (from the viewpoint of classical electrostatics) to be the most energetically favorable position for a cationic species to be located on the surface. For reference, the closest point of the white "lobe" to the ring oxygen atoms is on the order of 0.6 times the van der Waals radius of the atom. The dark isosurfaces therefore extend into regions of space that may be accessible to many cations. The negative lobes above each oxygen atom, combine to form a "ring" of negative potential on the surface of the clay above the oxygens. The electrostatic potential

Figure 2.2. Electrostatic potential for the silicate ring system in kaolinite.

in the ditrigonal cavities is also found to be negative but is considerably smaller in absolute magnitude. Empirical arguments about the chemical properties of the siloxane surface are thus in accord with the quantum mechanical findings.

In addition to the clean surface of kaolinite, we are now investigating the relative energetics of the physisorption of molecular HCl on the external (001) surfaces of both kaolinite and pyrophyllite.

Aqueous Surface Chemistry of MgO and $\text{Mg}(\text{OH})_2$

The reactions of metal oxide and silicate surfaces with water are among the most fundamental processes in geochemistry. In spite of the vast effort devoted to the study of solid surfaces, we have relatively little atomistic knowledge of the aqueous chemistry of oxide surfaces. It is not clear if water physisorbs as molecular H_2O , or dissociates by protonating surface oxygens and hydroxylating surface cations. The mechanism by which water adsorbs on oxide surfaces is of immense fundamental importance: For example, it is the first solvation layer on an oxide surface that determines how that surface will adsorb other species. Moreover, monolayers of water on mineral surfaces may profoundly affect the electrical properties of rocks. Presumably, such effects result from mobile protons on mineral surfaces and, hence, it is necessary to understand the degree to which adsorbed water molecules are dissociated.

Electronic structure (periodic Hartree-Fock) calculations were used to determine the mechanism by which water adsorbs on the surface of crystalline

MgO. Water is found to dissociatively adsorb on the (110) and (111) surfaces but not on the (100) surface (see also the work by Scamehorn, McCarthy, and Hess in the previous section). However, the dissociation of water on (100) is favored if the (100) surface is strained (as on an epitaxial layer). Dissociative adsorption of H_2O stabilizes the (111) surface. The mechanisms of adsorption on the MgO surfaces can be explained using classical electrostatic arguments.

The hydrolyzed (111) surface, the most stable, is the precursor to brucite $[\text{Mg}(\text{OH})_2]$. The calculated enthalpy of the $\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2$ reaction is 94 kJ/mol but decreases to 78 kJ/mol if the basis set superposition error (estimated with the counterpoise method) is included. The experimental enthalpy at 298 K is 80 kJ/mol. The close agreement with experiment suggests that proton transfer and phase transitions among ionic compounds can be reasonably treated at the Hartree-Fock level.

Proton Hopping in Minerals

On mineral surfaces, hydrogen bonds control adsorption processes and the structure of the surface solvation layer. Hydrogen bonds also allow protons to become mobile in minerals and on mineral surfaces. Thermally induced proton hopping has been proposed from the high-temperature IR spectra of some minerals. Proton hopping may be significant as an electrical conduction mechanism in the temperature regime of the earth's mantle and lower crust and is also an important consideration when using deuterium-hydrogen ratios in minerals to reconstruct geochemical processes.

The work discussed here is based on applications of the periodic Hartree-Fock LCAO code, CRYSTAL.⁽³⁾ The electronic structures of metal hydroxide and oxide-hydroxide phases are being calculated with 6-21G** and larger basis sets. The work done so far includes studies on brucite $[\text{Mg}(\text{OH})_2]$ and the AlOOH polymorphs. In brucite, each hydrogen is localized on a single oxygen atom. There are no real hydrogen bonds, and the MgOH sheets are held together by the dipole-dipole forces between opposing hydroxyl groups. In the AlOOH polymorphs, however, there is considerable delocalization of the hydrogen atom wave function onto next-nearest-neighbor oxygen atoms. The greater delocalization is consistent with the stronger Lewis acidity of Al^{3+} over Mg^{2+} . The lowest energy activation barrier for proton hopping in $\gamma\text{-AlOOH}$ is calculated to be only 0.57 eV. Such a low barrier implies that protons may be mobile at high temperatures.

Bulk and Surface Defects in Minerals: A New Electronic Structure Method

Defects play an important role in the bulk and surface chemistry of minerals. In fact, it has been argued that all of the interesting bulk and surface chemistry in these natural systems occurs at defect sites.⁽⁷⁾ The atomic and electronic structure of these active sites, however, is poorly understood, both experimentally and computationally. From a computational perspective, these sites are difficult to characterize because the loss of crystalline symmetry requires the use of a large unit cell, or a large cluster, and makes any first-principles treatment expensive. In band-structure (or *k*-space based methods) the use of a large unit cell containing the defect of interest (which is also periodically repeated) prohibits the study of charged defects which, in these methods, have a divergent Coulomb energy. The periodic repetition of the defects also makes the study of isolated defect properties difficult because of the large number of atoms that need to be included in the computation.

We have recently developed a real-space, first-principles, electronic-structure method, using the Harris-Foulkes energy functional and the recursion method, to compute the atomic and electronic structure of defects in mineral oxides. This approach overcomes the problems described above.⁽⁸⁾ Because the recursion method⁽⁹⁾ is used to solve the Schrödinger equation in real-space for *local* properties, the method is computationally efficient — we have performed computations on clusters of 27,000 atoms — and the need for supercell networks of periodically repeated defects is eliminated, allowing the examination of isolated and charged defects. This method has been tested and validated by computing the electronic structure and stability of the perfect (001), (111)-Mg, and (-1-1-1)-O surfaces of MgO and using the local-density of states at the surface to understand the relative stabilities and differing electronic structures of the surfaces in terms of the different surface chemical bonding.⁽¹⁰⁾ The results are in excellent agreement with other first-principles methods and with experimental results.

We have recently applied this method to the computation of the electronic structure and energetics of isolated bulk and surface oxygen vacancy defects (F centers) in MgO (see Figure 2.3). Based upon atomic relaxation principles first elucidated in the study of semiconductor surface reconstruction,⁽¹¹⁾ the atomic relaxation around these defects is expected to

Figure 2.3. Schematic indication of surface (F's center) and bulk (F center) oxygen vacancy defects in the rocksalt structure MgO. The surface shown is the (001) cleavage face. The small spheres represent magnesium atoms and the large spheres represent oxygen atoms.

be negligible. The computed formation energies of isolated surface and bulk oxygen vacancy defects are 1.16 eV and 1.82 eV, respectively, which are above the cohesive energy per formula unit. The computed formation energies are in excellent agreement with the available experimental data, which estimates a formation energy of 1.53 eV above the cohesive energy for the oxygen vacancy defect in the bulk material. Previous first-principles computations, using a supercell of 15 atoms (Mg_8O_7), arrived at a value of 0.4 eV.⁽¹²⁾ Clearly, the interaction of the defects in this computation is too large to ignore. The computed and experimental formation energies of these defects are in strong disagreement, however, with the pair potential model of an ionic material, which predicts a formation energy of 10.35 eV for a bulk oxygen vacancy. This disagreement can be explained in terms of the relaxation of the electronic wave function at the defect site that stabilizes the defect.⁽¹¹⁾

Chemistry and Physics of Metal Oxides

Phase Transitions in Oxides

Calculations of the total energy as a function of unit cell volume have been performed for ZnO in the wurtzite, zincblende, and rocksalt structures⁽¹³⁾ using the *ab initio* periodic Hartree-Fock LCAO method

described above. In an attempt to explore the dependence of various optimization schemes used in constructing the basis set, we have developed a new Zn basis (neutral and Zn^{+2}). This was done by first rescaling a recent Cu ionic basis supplied by N. Harrison (Daresbury Laboratory, Daresbury England), followed by an optimization of all exponents and coefficients for the neutral and +2 ionic states, subsequently followed by reoptimization in solid ZnO at the zincblende structure and the same experimental density as the equilibrium wurtzite phase. A standard oxygen basis set was also reoptimized for the zincblende structure.

Using the above basis set, the total energy was calculated at six to eight different volumes for each of the three structures. For the wurtzite structure, this required minimizing the total energy with respect to the structural parameters c/a and u at constant volume for each volume considered. The energy-volume relations for each structure (shown in Figure 2.4) were then fitted to the third-order Murnaghan equation, an empirical equation of state. Very accurate least squares fits were obtained in each case. These fits to an analytical formula were used to perform explicit analytical calculations of equilibrium volumes, bulk moduli and derivatives, phase transition pressure p_T (the slope of the tangent line in Figure 2.4), and free energies for the different phases. The calculated equilibrium geometries, equations of state, and

phase transition pressures are in excellent agreement with experimental results on the wurtzite phase, as shown in Table 2.1.

Table 2.1. Computed and experimental properties of ZnO.

	Zincblende	Rocksalt	Wurtzite	Expt'l.
$E_0 (E_h)^{(a)}$	0.0019	0.0089	0.0	
$V_0 (\text{\AA}^3)$	24.551	19.799	24.570	23.829
$B_0 (\text{GPa})$	156.8	203.3	154.4	140
B'	3.6	3.6	3.6	
c/a			1.593	1.603
u			0.3856	0.3823
$p_T (\text{GPa})$			8.57	9.0-9.5

(a) Energies relative to the wurtzite phase. Total energy of the wurtzite phase is $-1,852.70996 E_h$.

Equations of State and Pressure-Induced Phase Transitions of Oxides and Silicates

The reliability of the periodic Hartree-Fock method is being tested by calculating the equation of state of oxides and silicates and comparing the results to recent experimental measurements and to density functional calculations. The accurate prediction of elastic properties is necessary before we can reliably predict surface reconstruction and the energetics of defect and trace element substitutions. By comparing results with other theoretical methods, one can sort out effects resulting from basis set incompleteness and local, versus nonlocal, exchange and correlation. In Figures 2.5 and 2.6, the results of the periodic Hartree-Fock calculations (using the program CRYSTAL⁽³⁾) are compared with experiment⁽¹⁴⁾ and recently published local density approximation calculations.⁽¹⁵⁾

Provided an adequate basis set is used, calculated equations of state obtained with the periodic Hartree-Fock method are within 2% of experiment. Stishovite (rutile-structure SiO_2) is a useful example because it is the simplest noncubic silicate phase. An accurate equation of state requires that the c/a ratio and oxygen positional parameter be optimized at each volume. The resulting equation of state is in close agreement with experimental results taken under hydrostatic conditions and with recent FLAPW calculations. This work is being used to assess the reliability of theoretical methods applied to minerals.

Figure 2.4. Energy-volume relation for ZnO in both wurtzite and rocksalt structures.

Figure 2.5. *Ab initio* (periodic Hartree-Fock) equation of state for stishovite compared with experimental measurements and with recently published calculations using the local density approximation. The high-pressure data of Tsuchida and Yagi (1989) were not obtained under hydrostatic conditions so that agreement between theory and experiment is not expected.

Figure 2.6. *Ab initio* (periodic Hartree-Fock) equation of state for CaSiO_3 perovskite compared with experiment.

At the same time, theory is helping to interpret experimental results that are often controversial and uncertain.

Chemistry and Physics of Zeolites

Heterogeneous Catalysis in Zeolites

Zeolites are among the most industrially important compounds in use today. Naturally occurring as well as synthetic zeolites have applications in a wide variety of fields, including chemical separation processes, gasoline refinement, and long-term storage of nuclear waste products. The materials themselves possess an open-framework structure composed of SiO_4 and AlO_4 tetrahedra in conjunction with charge compensating cations. The TO_4 tetrahedra ($\text{T}=\text{Si}, \text{Al}$) in these porous materials interconnect by sharing corners to form one-, two-, or three-dimensional channels throughout the crystal; the structure of mordenite, which is typical of zeolites, is shown in Figure 2.7. The resulting system of "channels" allows these compounds to efficiently function as molecular sieves. In addition, the high internal surface area provides a large number of sites where processes such as ion exchange, adsorption, and catalysis can take place. Quantifying

Figure 2.7. Structure of the zeolite mordenite.

the effects that atomic scale properties (proton affinities, ion exchange capacities, etc.) have on the chemistry and reactivity of zeolites is a difficult experimental task. Traditional theoretical studies of the chemistry of zeolites have used either molecular dynamics simulations or *ab initio* calculations on molecular zeolite fragments to investigate such properties. These traditional approaches are limited by the quality of the force field employed or by the incorporation of unphysical effects into the problem by the truncation of long-range interactions.

The zeolites we have examined using the periodic Hartree-Fock method include zeolite A, mordenite, and silicalite. These materials represent some of the most widespread ion exchangers and catalysts used in industry today. Na_4Cl sodalite (and its fully siliceous form) have also been studied, and has potential applications as a conductive material. To provide a basis for future analyses of these aluminosilicates, initial studies were done on the siliceous forms of zeolite A, mordenite,⁽¹⁶⁾ and sodalite (silicalite has the same topology as ZSM-5, and already has the SiO_2 stoichiometry). The calculations have shown that the siliceous analogs of zeolites have very similar properties. The dominant character of the upper valence states is from oxygen 2s and 2p orbitals, with small contributions from silicon 3s and 3p orbitals. Framework bonding results from the overlap between the silicon 3s and 3p orbitals and the 2p orbitals of oxygen.

Evaluation of Mulliken populations indicates that charge is transferred from the silicon atoms to the oxygen atoms during crystal formation. Plots of the charge density and density deformation upon crystal formation show that there is little charge density in the center of the channels and large cages (e.g., the sodalite cage), and a concentration of charge density near the oxygen atoms. This electronic cloud is polarized toward the channel or cage center in an oblate shape relative to the spherical atomic densities. Evaluation of the electrostatic potential in the same region of the structure indicates that points near the oxygens are at a negative potential relative to the channel or cage centers. Plots of the electrostatic potential show lobes of negative potential about the oxygens directed towards the center of the channel. These arise from the nonbonding oxygen p-orbitals. All siliceous lattices investigated to date possess these characteristics. In these materials we therefore surmise that the most energetically favorable regions for cations in the lattices would be near the "walls" of the cylindrical channels and cavities, in the vicinity of oxygen atoms.

Ion exchange in Zeolites

The removal and containment of radioactive ^{137}Cs and ^{90}Sr from high level liquid waste is a critical problem for the cleanup of the waste stored in tanks at the DOE's Hanford Site. Many different materials have been proposed for the immobilization of such waste including borosilicate glasses, tailored ceramics or concrete, and zeolites. Historically, the containment of high level wastes in such materials has been hampered by the high leaching rates of the radionuclides from the host material. Recent experimental studies⁽¹⁷⁾ have shown that the open framework structure of several typical ion-exchanged zeolite lattices (e.g., Cs exchanged for Na in Na Zeolite-A) can be converted to less porous zeolites under hydrothermal pressing conditions. These "collapsed" zeolites (which typically possess the analcime structure) are observed to be thermally stable (melting point $>1700^\circ\text{C}$) with significantly reduced leaching rates. In essence, the original zeolite lattice collapses in a way that "shrink-wraps" the intercalated cations in the host lattice.

In order to investigate the transport rates of cations in these lattices, we have initiated *ab initio* studies of the diffusion of Group IA ions (Na^+ through Cs^+) through analcime type lattices. The aluminosilicate framework of these compounds is essentially unchanged by the presence of the various cations. The sodium form of the mineral is known as analcime, the potassium containing compound is called leucite, and the cesium analog is known as pollucite. By monitoring the total energy as a function of cation position in the lattice, the regions of the channels important to the diffusion process can be evaluated. With these data, transition state theory can be used to estimate the diffusion rates of cations in these lattices.

From the available crystallographic data it is believed that at equilibrium the cations in the analcime lattices are located in tube shaped cavities. Each end of the cavity is composed of a ring system consisting of six SiO_4 and/or AlO_4 tetrahedra. The direction of diffusion in these lattices is essentially one-dimensional due to large short range repulsion experienced in motion perpendicular to the cavity axis. Therefore, the cations are expected to move between tube shaped cavities by passing through a six-membered ring in the framework. Charge neutrality (or equivalently the attainment of a closed shell ground state) in these aluminosilicates is maintained via the presence of the group 1A cations.

Recently, we have completed total energy calculations on analcime and leucite. Figure 2.8 shows the variation in the total energy as the cation is moved from its equilibrium position in the center of the cavity (relative position 0.25 in Figure 2.8) through the transition state located in the center of the six-membered ring system (relative position 0.5). The results of these calculations indicate that for Na^+ and K^+ the barrier to migration is 0.5 and 4.1 Kcal/mol, respectively. Assuming the ratio of the vibrational partition functions at equilibrium and at the transition state to be unity, transition state theory allows us to predict that at 300 K the small barrier to Na^+ diffusion allows for the hopping of 0.4 cations per second through the six-membered ring. In effect, the Na^+ are moving freely throughout the lattice. For K^+ , the same estimate predicts a reduced hopping rate of 9.5×10^{-4} cations/sec. These results indicate a marked dependence of the rate upon the effective radius of the cation of interest. Current studies include calculations on the rubidium and cesium containing compounds where we expect the hopping rates to be reduced by orders of magnitude due to the size of the cation. In addition, we are evaluating the vibrational partition functions in order to more accurately estimate the diffusion rates.

Figure 2.8. Variation of total energy for cation migration through analcime and leucite.

Molecular Dynamics Simulation of Shape-Selective Separation in Zeolite Molecular Sieves: Butane and Isobutane in Silicalite

Shape-selectivity is key to the separation of hydrocarbon mixtures by zeolite molecular sieves. This fundamental aspect of zeolite chemistry is vital to the petroleum industry for the production of high-octane gasoline. Theoretical simulation of zeolite-adsorbate systems can provide insight into the factors that control shape-selectivity and the ways we can modify zeolite molecular sieves to enhance their efficiency.

We have simulated the diffusion of butane and isobutane in the molecular sieve silicalite using molecular mechanics and molecular dynamics techniques. The studies involve ensembles of 108 adsorbate molecules in a $3 \times 3 \times 3$ arrangement of silicalite unit cells. The total system contains 9288 atoms in a volume of $60 \times 60 \times 45 \text{ \AA}$. We have included all possible atom-atom interactions in the force field calculations. The adsorbate molecules have complete flexibility while the silicalite is held rigid. We have now run one nanosecond trajectories for two different concentrations of each adsorbate; the longest and largest simulations of these types of systems ever performed. The results show that isobutane diffuses significantly slower than butane; diffusion constants are 1.4×10^{-7} and $7.5 \times 10^{-6} \text{ cm}^2/\text{sec}$, respectively. This rather large difference in the diffusion constant demonstrates the shape-selective nature of zeolitic diffusion; the isomers have the same mass, but the branched isomer diffuses more slowly. Although the difference in diffusivities is large, it is still on the order of the accuracy of experimental measurements.

We also find the occupancy of the two isomers within the silicalite channels is significantly different. The butane molecules prefer to reside in the smaller channels in the zeolites that afford the most favorable van der Waals interactions with the zeolite. The more bulky isobutane molecules spend most of their time in the intersections between channel segments.

An important aspect of these simulations is that we used the power of the massively parallel Intel Delta computer. We now have a computer code to perform molecular mechanics, molecular dynamics, and normal mode calculations on parallel computers. The code is general purpose in the sense that it will run on a wide variety of workstations, networks of workstations, and parallel processors. It is also general purpose in the types of chemical systems it can treat, which includes gases, liquids, crystalline systems,

and proteins. The actual throughput on 512 computational nodes of the Delta is approximately 8 times that of a one-processor Cray Y/MP, permitting us to use larger ensembles of molecules and longer simulation times than were previously possible with available computer power. This greatly increases the statistical accuracy of the results.

Periodic Hartree-Fock Investigation of a Zeolite Acid Site

We have investigated the effect of placing aluminum and charge-neutralizing protons in a siliceous zeolite lattice using *ab initio* theoretical methods. Previous theoretical studies have been limited to clusters that mimic zeolite acid sites, while our calculations use the full periodic structure of the zeolite lattice. We therefore naturally incorporate the long-range electronic effects present in the true materials, leading to a significant improvement in our theoretical knowledge of zeolite acidity.

The calculations were performed using the program CRYSTAL.⁽³⁾ We used the siliceous analog of sodalite as the starting point for the calculations. This material has a composition of $\text{Si}_5\text{AlO}_{12}\text{H}$ after substitution of Al and the creation of bridging hydroxyl groups. All calculations were performed with the STO-3G basis set. The optimized geometry of the bridging hydroxyl group has a Si-O bond distance of 1.64 Å, Al-O distance of 1.72 Å, and a Si-O-Al angle of 136.3°. Interestingly, the charge is spread rather evenly throughout the system. For example, the Mulliken charge on Al is 1.272, while the charges on Si range from 1.399-1.446. The charges on the nearest neighbor oxygen atoms only vary by 0.228. This similarity in the electron density around Si and Al may account for the difficulty in crystallographically differentiating between these two elements.

Modeling Heteroepitaxial Growth of Materials

Combined Monte Carlo/Molecular Dynamics Model of Heteroepitaxy

A fundamental understanding of heteroepitaxial growth is important in many technologies, including the development of advanced electronic materials.⁽¹¹⁾ For example, understanding the formation of metal overlayers on compound semiconductor surfaces will provide valuable insight into a variety of complex metal-interfacial phenomena crucial to the intelligent design of electronic devices. The work in this project

focuses on the development of a quantitative microscopic model of the kinetic processes associated with heteroepitaxy. In particular, we use the formation of ordered structures of Column V (Sb, Bi) thin metal films on III-V compound semiconductor (110) surfaces as our test systems because of the wealth of experimental information available for both model development and assessment.^(11,18,19)

Theoretical studies of thermally-activated, elementary surface processes such as chemisorption, adsorbate migration, and desorption have employed a variety of techniques ranging from thermodynamic analyses to molecular dynamics and Monte Carlo simulations. The thermodynamic analyses suffer because only the energy differences between the initial and final states of the system are considered, ignoring the fact that these elementary reactions are most often activated processes.⁽²⁰⁾ Molecular dynamics and Monte Carlo simulations, on the other hand, suffer from the lack of computationally efficient, yet realistic, potential energy functions and from the inability to run sufficiently long simulation times. Indeed, for the simplest of potentials, reasonably achievable dynamic simulation times have been on the order of tens of picoseconds ($\text{ps} = 10^{-12} \text{ s}$), while macroscopic growth proceeds on a time scale that is nine orders of magnitude slower.

We have partially overcome the time scale problem with the development of a novel time-dependent Monte Carlo (TDMC) algorithm⁽²¹⁾ that allows us to eliminate the "rare-event" problem (i.e., spending many computer cycles "watching" a system in which no event occurs) and run simulations that are typically on the order of microseconds, reaching the diffusion limit for these processes. The potential we use for these simulations is the tight-binding, total-energy (TBTE) potential that has been successful in quantitatively describing the atomic and electronic structure, including atomistic dynamics, of the III-V(110) surfaces and the V/III-V(110) interfaces.^(11,18,19,22-24) This empirical, quantum-mechanical potential is sufficiently simple so that long simulation times of thousands of atoms on the surface are possible. Moreover, by incorporating realistic binding energies and barrier heights for surface processes, the accuracy of the TDMC simulations is optimized.

Our work, to date, has focused on developing the empirical TBTE potential for Bi/III-V(110) interfaces and on dynamical simulations of the ordering at the Sb/GaAs(110) interfaces. The Bi/III-V(110) potential is complete and has been successfully applied to the

Bi/GaAs(110) and Bi/InP(110) interfaces,⁽¹⁸⁾ with the computed atomic and electronic structures in excellent agreement with low-energy electron diffraction (LEED) intensity analyses and photoemission results. The preliminary results from the dynamical simulations are also in good agreement with experimental observations such as the preferential binding of Sb to the surface Ga atoms at low coverages, and the formation of islands at low coverages that coalesce into the ordered monolayer as the coverage is increased. The issue of preferential binding is an interesting one, since the computed binding energies indicate that the Sb adatoms are more strongly bound to the surface As atoms ($E_b = -2.7$ eV) than to the surface Ga atoms ($E_b = -1.5$ eV). Examination of the barriers to migration, however, reveal that while the As site is more stable, once a particle binds to the Ga site it is much more difficult for it to migrate to another site. As a result the trapping of Sb adatoms at surface adsorption sites is more effective at Ga sites than at As sites. This result most clearly illustrates the importance of including activation barriers in any dynamical model of surface processes.

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3. Biomolecular Modeling and Simulation

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Biomolecular Modeling and Simulation activities are currently focused on applying existing modeling/simulation methods and developing improved methods to uncover structure-function-dynamic relations of key biomacromolecules. The primary focus is to design new and improved catalytic functionality and/or alternative molecular properties of enzymes with an emphasis on developing near-, mid-, and long-term strategies specific for remediation and restoration of contaminated DOE sites. In order to develop a better molecular-mechanism-based understanding of the health effects associated with exposure to nuclear and chemical wastes, a secondary focus is on native versus perturbed DNA and recognition of perturbed DNA by essential enzymes. In this section, we describe some of our recent progress in our primary focus area.

The nature of deep contamination (commonly dilute, highly dispersed, and inaccessible) limits or precludes the application of many strategies that are currently being applied to remediate surface and near-surface contamination. Cost-effective remediation of synthetic substances in deep subsurface environments is for the most part limited to novel bioremediation alternatives.⁽¹⁾ The widespread use of synthetic organic compounds, such as halogenated hydrocarbons, has strained the capacity and, in some cases, exceeded the inherent functionality of naturally occurring biodegradative systems. Although microorganisms have tremendous capacity to evolve to meet new selection pressures, the time scale required to do so may be unacceptably long as measured by human time scales when hazardous substances are involved.⁽²⁾

The unique advantage of rational redesign is its ability to foster discovery of new enzymatic forms that would otherwise have an extremely low probability of evolving biologically under either laboratory-controlled or natural conditions. This is, in fact, to be expected for any enzyme requiring several simultaneous and specific amino acid changes to efficiently catalyze a significantly different substrate. To have a reasonable chance to successfully carry out a rational enzyme redesign study to alter an enzyme's specificity and/or improve its efficiency, certain enzyme

prerequisites are essential. For instance, it is necessary to have adequate enzyme structural data, an understanding of the mechanism(s) of action, and a cloned gene. Such information is available for the P450cam variant of the ubiquitous biodegrading and detoxifying superfamily of enzymes known as cytochromes P450.

Although experimentally determined enzyme structures are invaluable for understanding structure-function relations, the structural image obtained is an average in time and space. Nonaverage structural conformers, not resolvable by experimental methods, can also be important since bioactivity is not necessarily explainable from a consideration of an average structure. Many enzymes are thought to only transiently adopt functionally critical conformations; these transient conformations are not "visible" by today's high-resolution experimental methods. Computer simulations, starting from a high-resolution experimental structure, are expected to be capable of uncovering such structures. Experiments could then be designed to refute or confirm the significance of each transient population, in order to establish its role in bioactivity.

Collaborative experiment-theory studies with scientists at several universities are at different stages of maturity. Collaborative studies on cytochrome P450cam have been under way for about two years with Professor Steve G. Sligar at the University of Illinois/Urbana. In fiscal year 1992, we initiated a collaboration with Professors Dick B. Janssen and Bauke W. Dijkstra of the University of Groningen (The Netherlands) on the biodegradative enzyme alkane dehalogenase. Below we describe some of our recent studies to better understand structure-function-dynamic relations for cytochrome P450cam and to redesign its specificity and improve its efficiency.

Modeling The Dynamics of Enzymes

Dynamic Motions Associated with Buried Active Sites

The active site of cytochrome P450cam is deeply buried, and no direct experimental evidence is available regarding substrate/product motion from the exterior to the active site. The access channel(s) of P450cam is probably transient. Of the possible conformational mechanisms that could be dynamically responsible for substrate movement through the access channel, local "hinge-bending" is quite likely. Due to the large size of P450cam and lack of any direct experimental data on such motions, we have

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first focused attention on validating simulation methods for discovering such transient motions on one of the best studied smaller enzymes known to exhibit hinge-bending, T4 lysozyme.

A mutant form of T4 lysozyme has been observed to crystallize with four independent conformations in the crystal lattice, and hinge-bending motions are important to its catalytic mechanism.⁽³⁾ Figure 3.1 depicts five backbone superpositioned conformations of wild-type lysozyme from our recent 400-ps molecular dynamics simulation,⁽⁴⁾ which is qualitatively similar to the "hinge-bending" observed in the crystal. A more quantitative measure of the hinge-bending motions, using a dynamical cross-correlation method, also indicates significant and correlated motions occurring between the different domains.⁽⁴⁾ We are currently applying similar methods to gain a better understanding of possible hinge-bending motions in the biodegradative enzymes cytochrome P450cam and alkane dehalogenase (both have buried active sites).

Lock-and-Key Specificity in Cytochrome P450cam

Cytochrome P450cam hydroxylates camphor forming 5-hydroxycamphor with essentially 100% regio-specificity, while norcamphor is hydroxylated forming three products (45% 5-, 47% 6-, and 8% 3-hydroxynorcamphor).⁽⁵⁾ Our previous simulations of norcamphorbound P450cam predicted predominately (from 68% to 88%) 5-hydroxynorcamphor.^(6,7,8) One possible explanation for this discrepancy is that the simulations were performed using D-norcamphor, while the experiments were conducted with racemic norcamphor. The suggestion that norcamphor is the D-isomer was based on the similarity with the native substrate D-camphor. Indeed the reported crystallographic structure for norcamphor-bound P450cam models norcamphor as the D-isomer.⁽⁹⁾

Unfortunately, the two stereoisomers have never been separated. Three simulations each of the L- and D-isomers of norcamphor bound to cytochrome P450cam were compared to account for the affects

Figure 3.1. Backbone C-alpha atoms in T4 lysozyme when the N-terminal domain (residues 12-59, left) or C-terminal domain (residues 81-158, right) are superpositioned.

due to substrate orientation and the assignment of random velocities. Our recent results⁽¹⁰⁾ show that the L-isomer of norcamphor is predicted to give rise to predominately 6-hydroxynorcamphor, while the D-isomer gives rise to mainly 5-hydroxynorcamphor (see Figure 3.2). From this data, we infer that racemic norcamphor will give rise to nonracemic 5- and 6-hydroxynorcamphors after oxidation by cytochrome P450cam.

Redesigning Cytochrome P450cam

Before attempting to redesign the activity of P450cam for a substrate significantly different from camphor, we have chosen to first modify the specificity of P450cam for the substrate analog norcamphor. Achieving such an intermediate goal will give us considerable confidence and guidance towards modifying the specificity of P450cam to initiate the degradation pathway for targeted pollutants.

Modifying the Specificity of Cytochrome P450cam for Norcamphor

Molecular dynamics simulations of modified cytochrome P450cam have led to two mutants with enhanced specificity and efficiency for norcamphor. The activity of both mutants have been confirmed experimentally. The first involved mutating residue 87 based on the unexpected molecular dynamics simulation results indicating that this buried active site residue's very unusual dynamic mobility was correlated with the enzymes catalytic efficiency.^(6,11) Changing residue 87 from phenylalanine to tryptophan resulted in a 100% increase in coupling efficiency, in semiquantitative agreement with the prediction.⁽⁷⁾

The other successful prediction involved an alteration of specificity and efficiency of cytochrome P450cam hydroxylation of 1-methyl-norcamphor. The wild enzyme hydroxylates the 3, 5, and 6 positions of norcamphor, but only at the 5 and 6 positions of 1-methyl-norcamphor. For camphor, the degree of coupling is 100%, but for both norcamphor and 1-methyl-norcamphor, the efficiency is dramatically lowered to 12% and 50%, respectively. Based on modeling and simulation results, it appeared that mutating position 185 from threonine to phenylalanine would eliminate hydroxylation at the 3 position and dramatically

increase the efficiency (see Figure 3.3). This mutant was constructed and the product profile and efficiency experimentally determined. The efficiency was doubled and hydroxylation at the 3 position was essentially abolished; both in agreement with the prediction.⁽¹²⁾

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Figure 3.2. Paired stereographs of representative structures from the L-norcamphor and D-norcamphor simulations. The heme, pictured edge-on, and Tyr-96, which forms a hydrogen bond to the substrate, are shown. The individual heavy atoms of the substrate are labeled in each case. As can be seen, in the L-norcamphor simulation, the substrate adopts a position where the C-6 atom is closest to the heme iron (bottom), whereas in the D-norcamphor simulation, C-5 is the closest heavy atom to the heme iron (top).

Figure 3.3. Superpositional stereoviews of the active site of norcamphor-bound cytochrome P450cam. The energy-minimized active sites for wildtype (black) and mutant (gray). In the mutant, threonine 185 is replaced by phenylalanine.

4. Molecular Science Software

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Recent advances in computer hardware and software technology offer new opportunities to solve molecular-level problems of importance in environmental restoration and waste management, including key problems at the Hanford Site. Large scale parallel computing, high performance graphics, and integrated software applications environments are a few examples of emerging technologies with enormous potential for computational molecular science. The Theory, Modeling, and Simulation research and development program in Molecular Science Software (MSS) is focused on the application of such emerging computer technologies to theoretical and computational molecular science, in areas where significant advances in software technology are needed to fulfill the mission of the MSRC. This mission includes the development of improved theories and methods, software applications for modeling molecular systems, and applications for analyzing the results of molecular simulations. The MSS program contains components of software research, development, and engineering to provide high performance computing systems and software for the EMSL, computational methods and tools research for DOE's High Performance Computing and Communications Program, and exploratory research projects. Specifically to address these software needs, research and development projects have been undertaken to provide

1. efficient and effective implementations of advanced computational methods on a range of parallel computer systems, from clusters of workstations, to the high performance parallel

computer systems to be installed in the EMSL Molecular Science Computing Facility, to emerging teraFLOPS class computers

2. integrated and comprehensive application systems with modern graphical user interfaces to assist in the selection of computational parameters and provide chemistry-specific help for molecular simulations
3. visualization applications for analyzing the massive amounts of data obtained from large-scale molecular simulations, with an emphasis on the needs of the computer program systems developed in (1) and (2) above
4. knowledge systems that integrate computational models, interfaces, and databases to provide an efficient molecular modeling environment.

For essentially all computational algorithms in molecular science, multiple approaches are available. To support technical decision-making, MSS collects requirements from Theory, Modeling, and Simulation staff and other MSRC computational scientists, performs software prototyping and evaluations to clarify the objectives and technical approach, and either extends, implements, or integrates applications to meet the functionality required. Prototyping and implementation work often includes collaborations with external scientists, and embraces commercial and academic codes, as appropriate.

The following sections describe our accomplishments in 1992 and directions in each of the areas identified above, along with benchmark and calibration computations performed in support of this work. The most significant 1992 event for the MSS program was the official start of software design and implementation for the EMSL in July. At that point plans and concepts that had been developed over the past few years were finally being put into action.

High Performance Computational Chemistry Initiative

In 1992, we received funding from the DOE to pursue a new program in High-Performance Computational Chemistry. This project will be jointly performed by computer scientists and theoretical chemists at PNL and Argonne National Laboratory (ANL) with participation by the research laboratories of five industrial collaborators: Allied Signal, Inc., Amoco Research Center, E. I. DuPont de Nemours and

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Company, Exxon Research and Engineering Company, and Phillips Research Center. Our High-Performance Computational Chemistry program will develop the technology required to solve "Grand Challenge" class problems in computational chemistry. This project will develop the new algorithms, software, and diagnostics required to fully exploit the upcoming tera-FLOPS-class of massively parallel computers. In particular, algorithms will be developed that scale to larger numbers of processors, use hierarchical memory much more effectively, and make much smaller I/O demands than current methods. The goal is to develop modeling systems that are capable of solving problems orders of magnitude larger than currently possible. The work will focus on computational chemistry modeling methods appropriate to three specific problem areas of urgent interest to DOE and the chemical industry: the incineration of halohydrocarbons, the chemistry of clay minerals, and the rational redesign of biodegradative enzymes.

Parallel Applications for Molecular Computations

The development of accurate yet computationally tractable models of the mechanisms, energetics, and dynamics of molecular processes in the environment will require the development of new computer applications to both reduce the cost and extend the range of molecular simulations. Because the potential capacity and performance of large-scale parallel computer systems is well in excess of conventional supercomputers, these systems are becoming an increasingly important tool for molecular simulations. Full utilization of the computing capabilities offered by these machines will, in fact, be essential if we are to successfully pursue much of the work proposed in the EMSL (i.e., the modeling and simulation of molecular reactions, molecular spectra, and other molecular processes in solution, on surfaces, and at interfaces).

To realize the full potential of parallel computing, software must be developed that minimizes the amount of serial computations that must be performed, and maximizes the efficiency of the computations to be performed in parallel. Although the fundamental physics is well understood, and can be expressed at many degrees of approximation in models, little is understood about the best decomposition of the resulting equations on parallel computers. In addition, highly parallel computers present new

opportunities to model inherently parallel, coupled phenomena by more direct mappings of the physics.

Methodologies required by existing research programs in Theory, Modeling, and Simulation are

- Hartree-Fock-based electronic structure methods, including Generalized Valence Bond and second-order, Möller-Plesset perturbation theory
- higher order correlated methods, including CI and MCSCF methods as well as higher order perturbation theory and coupled cluster methods
- approximate Hamiltonian methods (e.g., semi-empirical or density functional)
- molecular dynamics.

Based on initial requirements analysis, the near term focus of MSS will be on the implementation of parallel quantum chemistry methods (the first three members in the above list) where little code is available that meets EMSL needs. A secondary emphasis will be placed on molecular dynamics, where we anticipate being able to extend and improve available applications codes for massively parallel computers from scientific collaborators and vendors.

Coupled-Cluster Methods for Parallel Computer Architectures: The Protomeric Tautomerism of 2-Pyridone and 2-Hydroxypyridine Revisited

The single and double excitation coupled-cluster method (CCSD), when augmented with a perturbational estimate of the effects of triple excitations (e.g., the CCSD(T) method), is arguably the most accurate closed-shelled electron correlation in routine application today. This method has recently been adapted for distributed memory parallel computer architectures.⁽¹⁾ The new algorithm is formulated in a semi-direct fashion, allowing contributions from integrals containing three or four indices in the virtual space to be evaluated directly from the integrals in the atomic orbital basis. This approach will allow these quantities to be recomputed during each iteration of the CCSD procedure rather than stored on external disk. As a consequence, the current I/O bottleneck and large disk requirement will be removed, allowing the method to be applied to significantly larger systems.

In addition to this formulation, the new algorithm distributes four index quantities containing one or two indices in the virtual space (e.g., the double excitation amplitudes) over the global memory of the

machine. On the Intel Delta, this has been implemented using the interrupt driven routine HRECV; and an interrupt handler on each node will send a copy of a particular portion of memory to a remote node as requested. Another interrupt handler has been used to load-balance the calculation.

The new code is currently being used to investigate the energetics of proton transfer reactions. Using the parallel direct SCF program DISCO,⁽²⁾ the structures and vibrational frequencies for several compounds have been determined. The relative energies of the compounds are now being determined using very large CCSD(T) calculations containing several million double excitation amplitudes.

One of the chemical systems of interest here is the protomeric tautomerism of 2-pyridone and 2-hydroxypyridine. The relative stability and the rate of tautomerism has recently been of considerable experimental and theoretical interest. This protomeric tautomerism reaction is considered to be prototypical of oxo-hydroxy tautomerization reactions in heterocyclic compounds. This reaction is also representative of certain nucleic acid base tautomeric processes that may be a crucial step in the mutation mechanism.

Past theoretical studies have used primarily semi-empirical methods (AM1, MNDO) with a few *ab initio* calculations at the SCF level and correlated levels of theory. The previous work has been limited to small or medium sized basis sets with few efforts that included polarization functions on the hydrogen atoms. The most significant work was that of Adamowicz.⁽³⁾ He predicted both vibrational spectra and intensities, as well as relative energetics with zero-point energy corrections. Adamowicz showed that hydrogen atom polarization functions are very important (even at the SCF level of theory) to the tautomeric process because of the interplay of the migrating hydrogen atom and the nitrogen and oxygen atoms. In the present study, the recent correlation-consistent polarized valence triple zeta (cc-pVTZ) basis sets developed by Dunning⁽⁴⁾ have been used to ensure that the effects of polarization functions are adequately treated. These basis sets have been shown to provide reliable energetics at the correlated level. For the 2-pyridone/2-hydroxypyridine system there are 280 basis functions with *s*, *p*, *d*, and *f* primitives. At the SCF level of theory, we have found the stable minimum of both species and the transition state for hydrogen migration. This allows us to predict the barrier height and the relative stability of 2-pyridone and 2-hydroxypyridine. The relative stability for this tautomeric system using the cc-pVTZ basis set and the SCF wave

function is 0.89 kcal/mol with the 2-hydroxypyridine being more stable. This is somewhat different than the Adamowicz result of 1.74 kcal/mole for smaller SCF basis set, but in line with other SCF predictions using Dunning's correlated basis sets. The SCF barrier height is around 50 kcal/mol. To date this is the first predication of the barrier to hydrogen migration for this system. CCSD(T) calculations will be used to predict the relative energetics at these critical points on the potential energy surface and afford a more reliable prediction of the stability and barrier height.

Massively Parallel Full Configuration Interaction Program

The full configuration interaction (FCI) method provides the exact solution of the nonrelativistic, Born-Oppenheimer Schrödinger equation within a given one-particle basis set. The ability to compute FCI results enables accurate assessment of errors in lesser models of electron correlation, in the one-particle basis set, and in the wave function. Currently, FCI computations are constrained by the volume of both computation and data, and much larger FCIs are still needed, particularly for transition states, extended systems, response properties and metallic clusters, which have been little studied at this high level of theory.

The currently most efficient FCI algorithm,⁽⁵⁾ which is fully spin-adapted, serves as a valuable prototype of more complex CI algorithms and as the heart of a CASSCF program. This parallel FCI code is intended to use massively parallel computers to partially address the need for large FCI benchmarks, and also to explore issues in parallelizing complex CI algorithms. These latter issues include manipulation of large, distributed data structures, scalability, and portability.

Work commenced on the FCI program while R. J. Harrison was at ANL with E. A. Stahlberg (a PNL postdoctoral fellow). Since then, the program has been tuned and extended to compute the one-particle density matrix and natural orbitals, and to page the CI vectors to and from disk. The code functions on the Intel Touchstone Delta (using message passing), the Alliant FX/2800 (using shared memory and fork/join) and the Alliant FX/2800 and Cray computers (using compiler directives). The paging makes it essentially open-ended, although there is a big performance penalty on machines such as the Delta, with I/O performance incommensurate with their computational power.

Figure 4.1 shows the speed-up of the performance of the code on the Intel Touchstone Delta for several problems. The largest problem run to date is methane (carbon 1s frozen) in a cc-pVDZ basis,⁽⁴⁾ which included 94,930,032 configurations (418,639,400 determinants). This calculation takes just 226 seconds to perform one iteration. During each iteration, on 512 nodes, it performs 0.9×10^{12} floating-point operations and sends 4.2 million messages with a total volume of 34 Gigabytes.

Calculations on the geometries, harmonic frequencies, and dipole/polarizability derivatives of methane and the methyl radical in a cc-pVDZ basis commenced at ANL and have continued at PNL.

These proof-of-concept and benchmarking calculations have provided insights into the deficiencies in current performance models (e.g., the need for stochastic modeling of dynamically balanced parallel programs) and the Delta operating system (e.g., poorly specified system behavior, multiple bugs), and demonstrate that a high-level, object-based design can result in a portable, high-performance program. In addition, the calculations are the largest such calculations yet performed and provide valuable theoretical benchmarks.

Work is now under way to incorporate this program into a massively parallel CASSCF code.

Figure 4.1. Performance of the massively parallel FCI code on the Intel Touchstone Delta for several different problem sizes.

Parallel Full-Potential Linearized Augmented Plane Wave Calculations

We are developing a parallel implementation of a total-energy, full-potential, linearized-augmented plane wave (FLAPW) method for bulk solids. This method solves the Kohn-Sham local density functional equations to determine the physical and electronic properties of the ground state of many atom systems.⁽⁶⁾ The charge density, potential and crystal orbitals are expressed within the interstitial region in terms of plane waves that are augmented by spherical harmonic expansions within spheres centered on the nuclei. The implementation is targeted for massively parallel processing architectures such as the Intel Touchstone DELTA supercomputer. The parallel program will be used to study the electronic structure and physical properties of complex crystal systems of interest in understanding the transport and transformation of contaminants in soils and groundwater.

Parallelization of this method first requires a consideration of its memory requirements. For instance, calculations for a relatively simple crystal such as silica sodalite, require 50-100 Mbytes of memory using accurate basis set expansions that approach 100 augmented plane waves per atom. Since memory per processor is limited, much effort is required to distribute data structures in order to efficiently exploit the large aggregate memory of massively parallel computers. A distributed data model also eliminates any need to temporarily store data on disk and the consequent I/O bottlenecks. Our initial design reserves 6 out of 12 Mbytes of usable memory per node on the DELTA for program temporary data space. As memory increases on future massively parallel computers, distribution of data structures will remain critical as calculations on larger systems are conducted.

An iterative solution of the Kohn-Sham equations generally has three components: potential computation, a generalized eigenvalue problem, and charge density computation. The total potential of the FLAPW algorithm has been largely parallelized, while work is progressing towards fully parallelizing the remaining two components. Figure 4.2 presents the elapsed time required to solve Poisson's equation for the Coulomb potential, V_c , as the number of processors increases. Distributing the data structures allows storage of results computed initially for later use. In the case of V_c , this decreases the work by an order of magnitude for iterations after the first.

Figure 4.2. FLAPW timings for an SCF iteration on silica sodalite. Grid parameters are 4 K-space points and $G_{\max}^1 = 1.5 a_0$.

Figure 4.2 also shows the ideal elapsed time decrease (dotted line) starting from the initial point of the plot. Comparison of actual and ideal timings indicates excellent efficiency (i.e., ≈ 90 percent) for the parallel computation of V_c . The exchange-correlation potential scales equally as well.

Accuracy of the FLAPW solution primarily depends on the number of basis functions in the plane wave expansions. As the number of augmented plane waves increase, the eigenvalue problem increasingly dominates the calculation. Its solution requires diagonalization of dense, symmetric matrices to obtain a small fraction of the total eigenvalue spectrum. For a set of points in the 1st Brillouin zone, the eigenvalues are determined by defining variational equations that neglect the nonspherical part of the potential within the atomic spheres. The eigenvectors of this 1st variation comprise the basis set for a 2nd variational set of equations incorporating the total potential. Figure 4.2 illustrates the poor efficiency attained ($\approx 50\%$) even for a small basis set when a sequential eigenvalue solver is used in this 2nd variational step. In collaboration with R.J. Littlefield and G.I. Fann of

PNL, a distributed, parallel eigenvalue solver is currently being incorporated to improve the performance. The eigensolutions are determined using a bisection plus inverse iteration scheme. Once this has been fully integrated, the projected efficiency of the program should approach 75 to 85%.

An Implementation of the Direct SCF and RPA Methods on Loosely Coupled Networks of Workstation

Distributed or cluster computing using very fast reduced instruction set chip (RISC) based workstations is becoming a viable alternative to the typically overloaded centralized supercomputer centers. RISC-based workstations are extremely cost effective for computational chemistry, based on price and performance issues. Moreover, these machines can often deliver more throughput than the small fractional share traditionally allotted to users on a supercomputer. In fact, several supercomputer centers are pursuing or using clusters of RISC-based workstations to off-load a large fraction of their scalar computations. In the past, groups of workstations have been used as a resource pool for a series of sequential jobs, but with the advent of message passing software systems such as PVM,⁽⁷⁾ TCGMSG,⁽⁸⁾ Network Linda,⁽⁹⁾ and ParaSoft Express,^(a) a cluster can also work together on a single problem. While this use of clusters is less efficient than running the jobs in a serial fashion, increased throughput can be obtained for time critical applications. Additionally, workstation clusters are very attractive, cost effective, parallel software development platforms. With suitable tools, an application can readily be developed on a group of workstations and then straightforwardly ported to moderately parallel machines (~ 100 nodes) by only making changes to the software that are inherent to the different FORTRAN and/or C compilers. If the implementation of the application algorithms scales properly, then software for massively parallel machines can also be developed on the cluster platform.

The distributed cluster environment also affords researchers the opportunity to utilize large amounts of computing resources from idle workstations during off-hours. The purpose of our work is twofold. First, we have implemented a version of a quantum chemistry program that can be used on both clusters and parallel computers. Second and of equal importance,

(a) A. Kolawa, a ParaSoft representative, private communications.

we have used the program to study the first-order response properties [e.g., the polarizability, $\alpha(E)$] of parnitroaniline (pNA).

The pNA monomer molecule contains 10 heavy atoms and 6 hydrogen atoms (see Figure 4.3). The structure used for the pNA calculation was taken from reference⁽¹⁰⁾ where its optimization is described. The cyclopropenone molecule C_3H_2O was used in previous work to develop a basis set for subsequent use on the parnitroaniline molecule and its dimer. Exploratory work was carried out to determine an basis set that was capable of predicting $\alpha(E)$ to an accuracy of $\pm 10\%$ and that was computationally feasible for use on the pNA monomer and dimer. Using the 0P basis, as described in reference⁽¹⁰⁾, the calculation on pNA required 148 primitive Gaussian atomic orbitals. At the optimized geometry, the energy and dipole moment of the pNA monomer are $-486.750276 E_h$ and 2.901D, respectively. The components of the static polarizability $\alpha(E=0)$ are computed to be $\alpha_{xx} = 90.7$, $\alpha_{yy} = 37.0$, $\alpha_{zz} = 121.3$, and $\alpha_{av} = 83.0$ in atomic units.

The calculation of $\alpha(E=0)$ required 30 iterations to converge the SCF solution and 18 iterations to converge the RPA equations. This represents 48 passes through the two-electron integral evaluations. All calculations were performed on a 'stand-alone' cluster of four IBM RS/6000, Model 520 workstations networked through 16-Mbit token ring connections. Each workstation was identically configured with 64 Mbytes of memory and 1 Gbyte of disk running AIX 3.1/XLF 2.0. Sequential calculations performed on an individual workstation had a run time of $23,886 \pm 78$ seconds. This same calculation took 7962 seconds for the 1 master and 3 slave workstations and 5972 seconds for 1 master/4 slaves. To put this into perspective, this same calculation required 5040 seconds to run on

Figure 4.3. pNA Monomer $O_2N-C_6H_4-NH_2$.

an IBM 3090, Model 600vf. In addition, a 1 master/3 slaves calculation was run on 4 processors of an Intel iPSC/860 (gamma) resulting in a runtime of 14,101 seconds.

Graphical User Interfaces for Computational Chemistry Codes

Modern graphical user interfaces (GUIs) have proven to be both convenient and powerful, substantially reducing the learning time required to run complex application programs, while providing broad access to the computational power of the computer system. GUIs for the large, complex computational chemistry codes used today would greatly facilitate the use of these codes for molecular simulations, and provide much needed assistance to researchers who are not experts with a particular code or method. GUIs would

- reduce the time required to prepare the data input
- reduce the errors that arise in the preparation of the data input
- facilitate the analysis of the data generated in the simulations.

GUIs also provide the foundation for both the graphical analysis of the results from molecular simulations and the integration of discrete computer programs into a comprehensive, problem-oriented package.

Graphical User Interfaces for Electronic Structure Codes

During 1992 work has continued on the prototype GUI for computational chemistry applications, known as the Computational Chemistry Input Assistant (CCIA). This interface currently supports the widely-used GAMESS⁽¹¹⁾ *ab initio* electronic structure package. GAMESS offers a large set of computational models for describing molecular processes. As a consequence, it has several hundred input parameters, some of which are unique to GAMESS and all of which possess their own unique syntax. A goal of CCIA is to allow scientists to perform their calculations without having to learn a lot of application-specific information. This should enhance the scientist's ability to migrate from one application to another as their research needs vary throughout the course of a project. An example of a screen from CCIA is shown in Figure 4.4.

A larger fraction of the methods in GAMESS are now supported by CCIA, and more options are available

Basis Sets (Seek Advice)

INFO

Information Desired From This Calculation

☒ Molecular Structure	0.60	<div style="display: flex; align-items: center;"> <div style="flex-grow: 1; border-bottom: 1px solid black; position: relative;"> <div style="position: absolute; right: 0; top: -5px; width: 10px; height: 10px; background-color: black;"></div> </div> </div>	W E I G H T
☐ Vibrational Modes		<div style="display: flex; align-items: center;"> <div style="flex-grow: 1; border-bottom: 1px solid black; position: relative;"> <div style="position: absolute; right: 0; top: -5px; width: 10px; height: 10px; background-color: black;"></div> </div> </div>	
☒ Relative Energetics	0.40	<div style="display: flex; align-items: center;"> <div style="flex-grow: 1; border-bottom: 1px solid black; position: relative;"> <div style="position: absolute; right: 0; top: -5px; width: 10px; height: 10px; background-color: black;"></div> </div> </div>	
☐ Moments/Polarizabilities		<div style="display: flex; align-items: center;"> <div style="flex-grow: 1; border-bottom: 1px solid black; position: relative;"> <div style="position: absolute; right: 0; top: -5px; width: 10px; height: 10px; background-color: black;"></div> </div> </div>	
☐ Transition Moments		<div style="display: flex; align-items: center;"> <div style="flex-grow: 1; border-bottom: 1px solid black; position: relative;"> <div style="position: absolute; right: 0; top: -5px; width: 10px; height: 10px; background-color: black;"></div> </div> </div>	
☐ Spin Density Properties		<div style="display: flex; align-items: center;"> <div style="flex-grow: 1; border-bottom: 1px solid black; position: relative;"> <div style="position: absolute; right: 0; top: -5px; width: 10px; height: 10px; background-color: black;"></div> </div> </div>	
☐ Excitation Energies		<div style="display: flex; align-items: center;"> <div style="flex-grow: 1; border-bottom: 1px solid black; position: relative;"> <div style="position: absolute; right: 0; top: -5px; width: 10px; height: 10px; background-color: black;"></div> </div> </div>	

← Less More →

Criteria for Making Recommendation

Overall Accuracy ☒ Low ☐ Medium ☐ High	Level of Theory ☒ Hartree-Fock ☐ Correlated	Ability to Reproduce ☒ Experiment ☒ Best Available Theory	Consider: ☒ Accuracy & Speed ☐ Accuracy Alone ☐ Same Charge Only
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Proceed

Figure 4.4. A sample screen from the Computational Chemistry Input Assistant, a prototype graphical user interface.

for carrying out common tasks, such as specifying the molecular geometry. A formal usability study, involving MSRC scientists and a selected set of tasks, has been conducted on the prototype interface in order to help guide the development of the first UNIX-based interface.

CCIA's advanced help facility, which can recommend appropriate basis sets for various areas of interest and levels of theory, has been extended to now include the results of roughly 1500 calculations on small-to-medium size molecules. In collaboration with other members of the MSRC staff, the database of computational results has been augmented with extremely high level calculations coming out of research with the correlation consistent basis sets.

Visualization and Analysis of Molecular Simulations

The emergence of the high performance desktop graphics workstation is sparking a revolution in graphical data analysis. Visualization, once a time consuming and tedious post-analysis tool, is fast becoming the tool of choice for routine interactive

data analysis. Although several capable general visualization software packages exist, a large software gap exists between their functionality and the integrated science-specific visualizations required to extract the salient data attributes in the most insightful manner for molecular science applications.

MSS work in this area is targeted at the development of molecular visualization applications for analyzing the massive amounts of data obtained from large-scale molecular simulations, with a focus on key Theory, Modeling, and Simulation computational modeling methods. This work requires an intimate understanding of the data analysis problems encountered in MSRC research. Extensive interaction with representative scientists and specific science problems reveals opportunities for assisting the research process with visualization. Next, prototype software provides a basis for evaluating trial visualizations on real data and valuable insights leading to new visualization approaches that are applicable to broad classes of modeling and simulation data. In the implementation stage, visualization applications are constructed and integrated in a seamless molecular science software environment.

Graphics and Visualization of Crystals

Prototype code development in the AVS environment has recently targeted the creation of AVS modules that enhance our ability to model and analyze crystal-line materials. Of particular importance is addition of the ability to determine the space group of highest symmetry of a given set of atomic coordinates. Utilizing the highest symmetry in quantum mechanical computer codes can greatly reduce the amount of computation necessary. We need this ability both for new materials we wish to model and to modify existing crystal structures.

We developed this suite of AVS modules as independent from AVS as possible, isolating the computational routines in standard C functions and grouping them into a UNIX library. The AVS modules make calls to the C functions and are linked to the functions at compile time through the library. In addition, we have written programs in C to test the accuracy of each of the chemistry functions independent of AVS. In this case, we write the results to the UNIX standard output, rather than to the AVS windowing system. By isolating the chemistry functions, porting this software to other visualization systems will require minimal effort.

In addition to the crystallographically oriented code, we have written or modified other visualization code for crystals. We modified the popular Connolly Dot Surface program to correctly treat crystal systems of any symmetry. Connolly surfaces are often very time consuming to generate, however, they are very attractive for presentation purposes. For less demanding visualizations, we have developed a new method for generating dot surfaces, and have linked that with an implementation of the marching cubes algorithm to generate isosurfaces. We have written code to generate electrostatic surfaces from various point charge models, and display these as shaded isosurfaces. We can apply all of the work with electrostatic surfaces to crystal systems, and this code development complements work by other groups in understanding the electronic properties of crystals with quantum mechanical methods.

Although we are evaluating other software platforms for the implementation of our final product, AVS continues to be a strong part of our prototyping environment. New enhancements to AVS, such as the module generator, greatly aid the prototyping process. The module builder also automatically produces a

template for documenting each new module. The use of the module builder by each member of the team promotes consistency in code appearance, greatly simplifying code maintenance.

Integrated Computational Chemistry Environment

Most molecular simulations are carried out in a piecemeal fashion. For example, calculation of the infrared spectra of a molecule requires a multistep process, each step of which requires execution of a distinct set of programs and each step of which may depend on the output from earlier steps.

Calculation of the dynamics of a chemical reaction requires a similar multistep procedure. Advances in computer technology, computer science, and computational methodology provide the foundation for developing program systems that combine all of the needed elements into one integrated, comprehensive package.

The initial focus has been on completing a high-level design of an extensible, application-to-application protocol for molecule information that supports facile creation of molecular science software application interfaces, and execution of complex computational "experiments" in a heterogeneous, distributed, computing environment. As design objectives are refined, we will create prototypes to demonstrate key sections of this design.

Software Strategies for an Integrated Computational Chemistry Architecture

Over many years of development, accurate computational chemistry codes have evolved into large comprehensive packages requiring computational resources far in excess of those available on the desktop today and in the foreseeable future. Integration of these codes along with advanced user interfaces, new visualization tools, and persistent data storage systems in a highly integrated environment are limited by the absence of a robust data model that facilitates interaction of these components. Our purpose is to develop an integrated computational chemistry architecture (ICCA) that consists of a data model and associated knowledge server capabilities to promote this level of integration in a distributed heterogeneous computing environment. Also, the ICCA will allow us to further abstract computational chemistry to the level of chemistry experiments; in other words, to perform complex

computational experiments involving groups of molecules utilizing many applications to achieve a desired outcome.

The initial phase of this project has consisted of a data model design involving a collaborative team of both computational chemists and computer scientists from PNL, CAChe Scientific Inc., and Oregon Graduate Institute. The data model describes research chemistry (as applicable to computational chemistry) in terms of its important entities (objects) and their relationships. A knowledge server will be designed around this high-level data model to allow for ICCA-compliant applications (user interfaces, visualization systems, computational codes, database systems) to access data and resources through a common chemistry specific dialect, immune from specific data formats. The ICCA design strategy stresses that applications need to communicate via the natural objects of a distributed computational chemistry-specific environment and understand the behavior of these objects rather than impose specific low-level data formats throughout the entire system. The knowledge server will make available capabilities for (but not limited to) construction, storage, retrieval, and computation of high-level objects such as molecule, procedure, and calculation objects. The design of the ICCA embraces some of the latest concepts in information systems, including object oriented techniques that should produce a more extensible and maintainable system than traditional approaches. High-level management of computational chemistry experiments, via this object-oriented approach, is a key goal of this project. We also hope to facilitate the definition of widely acceptable objects useful to quantum chemistry.

Benchmark Computations

Systematic studies of the accuracy of computational methods are of vital importance to the design of simulations in the MSRC and elsewhere. Some methods are poorly calibrated in the domains of interest to our program, and in many cases the computational resources are only now becoming available to carry out the studies necessary to explore the limits of an approach. To optimize the deployment of our software development resources, we carry out targeted series of benchmark and calibration computations that provide evaluations and parameters to guide MSS methods and applications development.

Because the amount of computer time, high-speed memory, and disk resources vary enormously with

the choice of parameters, it would be very useful for scientists to have access to detailed information about the performance of different computational models, so they can make informed decisions concerning the efficient use of computer resources while still obtaining results with sufficient accuracy to solve the problem at hand. To realize this goal, the CCIA is being designed to provide facilities to assist scientists in making complex decisions regarding the large number of input parameters that control how the chemical modeling application will work. These capabilities are driven by a database documenting the performance of various computational models. While part of the needed information can be obtained from the chemical literature, certain important pieces of information are missing and must come from our own benchmark calculations.

Methods to Estimate the Complete Basis Set, Full CI Limit

By combining two empirically-motivated exponential fits it has been shown, in a limited number of cases, to be possible to extrapolate to the exact solution of the most commonly used form of the time-independent molecular Schrödinger equation (i.e., the complete basis set, full CI limit). Due to the factorial growth in the size of full CI calculations with the number of basis functions and number of electrons, it is currently impossible to carry out such calculations with extended basis sets. Because our proposed method scales much less drastically with the size of the problem, it offers hope for obtaining reliable estimates of the complete basis set, full CI limit that will be used for calibration of more approximate methods.

The first of the two exponentials represents the convergence of the total energy (or a generic property) as a function of the one-particle basis set completeness. The other exponential represents the convergence with respect to the n -particle basis set or degree of correlation energy recovery. The sequence of wave functions used in this prescription employs the correlation consistent basis set family and a systematic set of MRSD-CIs. Tests on the water molecule with basis sets including up through h functions have demonstrated the practicality of this approach for a wide assortment of energy-related and 1-electron properties (see Figure 4.5). Although exponential convergence of the one-electron properties is not universally observed with this approach, in the majority of such cases where it fails to appear, the property in question was already

Figure 4.5. Convergence of the estimated full CI energy as a function of the size of the correlation consistent basis set. The solid line represents an exponential fit of the available data.

nearly converged. For the water molecule, the estimated complete basis set, full CI valence correlation energy agrees to ± 1 millihartree with an estimate based on the experimentally observed binding energy.

Ab Initio Studies of Hydrogen Bonding

Due to the size of the molecular systems involved, the modeling of environmental processes often requires scientists to resort to empirical force field methods. Nonetheless, *ab initio* methods may play a role in providing high quality data that is unavailable experimentally and that can be used as input to calibrate the force field. In this vein, high-level *ab initio* calculations were performed on the (hydrogen bonded) phenol-water complex. Phenol is representative of a class of aromatic alcohols present as soil contaminants at nuclear materials processing sites.

Geometry optimizations at the second order Møller-Plesset perturbation theory level using polarized basis sets were performed in order to identify minima

on the potential energy surface. Three of these persisted as the level of theory was increased and one disappeared. Two of the persistent minima are shown in Figure 4.6. Counterpoise corrected energies were subsequently evaluated using a basis set containing multiple sets of polarization functions on all atoms. The effects of extending the basis set another level, to include multiple sets of *f*-functions on the first row atoms and multiple *d*'s on hydrogen, was estimated through calculations on a smaller prototype system. Electronic binding energies and enthalpies of formation indicate that one of the complexes is more strongly bound than the water dimer (by ~ 3 kcal/mol), one is equal to the dimer and one is only half as strong as

Figure 4.6. The two lowest energy conformations for the phenol-water hydrogen bonded complex. Bond lengths and angles are from *ab initio* electronic structure calculations at three levels of theory - A: HF/3-21G, B: HF/6-31G**, and C: MP2/6-31G**.

the dimer. The findings of this work will be used in further studies involving multiple waters interacting with phenol.

A Density Functional Study of the Structure and Acidity of Hydroxyl Groups in Molecular Sieves

Zeolites are aluminosilicate frameworks that contain networks of cavities that permit the transport of a range of molecules and ions relevant to environmental and catalytic processes. Zeolites typically have 100-800 atoms in a unit cell. Therefore, a quantum mechanical study of the electronic structure and physical properties (e.g., relative acidities) of these systems using Hartree-Fock methods is very computationally demanding. Density functional methods are a viable alternative to Hartree-Fock methods since their computational demands scale more economically with systems of increasingly larger size.

The physical properties of zeolites and related materials can often be understood by studying small prototypical systems. To assess the applicability of a density functional approach to zeolites, the structures and relative acidities of a series of molecules that mimic terminal and bridging hydroxyl groups in various zeolite molecular sieves have been calculated by local density functional (LDF) methods. Of primary interest is disiloxane, $\text{H}_3\text{Si-O-SiH}_3$, and its protonated form, $\text{H}_3\text{Si-OH-SiH}_3^+$. Also studied are structural analogs of disiloxane where Si is substituted isoelectronically by Al, B, P, Ga, and Ge. Silanol, $\text{H}_3\text{Si-OH}$, the simplest model of terminal hydroxyl groups at zeolite surfaces and defect sites, is also included. The LDF structures and acidities, calculated with the program DMol⁽¹²⁾ using a range of numerical basis sets and quadrature grid sizes, have been compared with Hartree-Fock/MP2 results. The effect of nonlocal density functionals on the structure of disiloxane has also been examined using the deMon program.⁽¹³⁾

The study indicates that optimized geometries, particularly the T-O-T bond angle (T = tetrahedrally coordinated atom), are sensitive to basis set size as well as the level of electron correlation described. Figure 4.7 shows the variation of the optimized T-O-T bond angles over a range of basis sets and grids. LDF predictions using the extended basis set underestimate the bond angle.

Nonlocal functionals correct this discrepancy. Differences between the LDF and HF/MP2 T-O bond lengths correlate with bond strength. Very good

agreement is observed for the stronger Si-O and P-O bonds, while LDF predicts significantly shorter bond lengths for weaker bonds such as B-O. Bond lengths involving hydrogen are systematically too large although the O-H bond lengths markedly improve with an extended basis set. The theoretical trend in acidity of terminal and bridging hydroxyls, as determined by the proton affinity, agrees with the experimental trend observed for isomorphically substituted ZSM-5 zeolites.

The LDF approach provides results of comparable accuracy to Hartree-Fock/MP2 calculations at reduced computational expense. For instance, a single point energy calculation for $\text{H}_3\text{Si-O-AlH}_3$ is roughly four times faster with the DMol program than a Hartree-Fock/MP2 calculation using the Gaussian-90 program.⁽¹⁴⁾ The difference in time required for a force calculation should favor the LDF method even more. In certain instances, LDF theory overestimates weak binding interactions although nonlocal functionals appear to correct this deficiency, albeit at greater computational expense.

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Figure 4.7. Variation of optimized T-O-T bond angles over a range of basis sets and numerical quadrature grids of increasing size in the local density functional program DMol.

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Computing and Information Sciences

Computing and Information Sciences

Computing is an integral part of the research being conducted by scientists in the MSRC. The advanced computing infrastructure for the EMSL will provide state-of-the-art computing for this facility where scientific research can be performed to support DOE missions in environmental restoration and waste management, energy and environmental quality, and science and technology.

The research and technology development elements of the MSRC Computing and Information Sciences program are aimed at providing technical solutions to problems defined by the theoretical and experimental research programs that support DOE missions. Activities in this program include software development for graphical user interface and visualization, development of parallel methods for computational chemistry, and development of data storage systems that provide easy access to pertinent scientific data. There is an emphasis on laboratory automation, including instrument control and data acquisition technologies and telecomputing, through which remote collaborators can participate via the network in the planning, execution, and analysis of experiments. The network infrastructure and distributed computing are areas of technical importance to the efficient operation of the EMSL.

1. High-Performance Computing

**R. J. Littlefield, G. S. Thomas, G. I. Fann,
A. B. Shiflet, and K. J. Maschhoff**

The purpose of the high-performance computing program is to provide computer science support to the task of exploiting the fastest available computers for computational chemistry. The primary objectives of the program are to develop analysis and programming techniques that will expand the range of applications for which parallel supercomputers can be used effectively, and to develop evaluation criteria by which computer systems can be designed and selected for use by the MSRC. In particular, the program includes research and development to

- develop techniques for predicting and evaluating the performance of a scientific code on a parallel computer

- evaluate alternate strategies for programming computational chemistry applications
- develop efficient implementations of kernel computations that are important for computational chemistry
- determine which parameters of a parallel computer system are most important to chemistry applications
- improve those parameters in future computer systems.

Approach

The high-performance computing program involves a combination of theoretical and experimental work on large-scale parallel machines. The work focuses on kernel computations for which existing tools and techniques fail to fully exploit the capabilities of parallel machines. The major components of this approach include

- studying kernel computations chosen to expand the current capability of parallel machines
- developing performance models for those kernels
- improving kernel algorithms
- developing and evaluating tools and techniques for performance modeling and visualization, and programming parallel applications
- participating in the CSC
- performing operating system research and vendor collaborations regarding critical parameters of parallel computer systems.

Activities and Results

The work in 1992 focused on two major computational kernels: eigensolution of dense symmetric matrices (needed for electronic structure calculations), and global vector sum (needed for molecular dynamics using the replicated data strategy). Both of these kernels are demonstrated bottlenecks in practical applications and have proved difficult to implement efficiently on massively parallel machines. In each case, performance modeling techniques have been

used to understand the tradeoffs between alternate algorithms and the effect of computer characteristics on performance. New algorithms have been developed, modeled, and studied experimentally on large-scale parallel machines such as the Intel iPSC/860 and Touchstone DELTA. This work has resulted in the development of faster algorithms and improved methods for modeling and characterizing parallel machines and programs. These results are described in more detail in the next section on parallel computational kernels.

Staff from the Computing and Information Sciences program have been active members of the CSCL DELTA project team. Staff from the MSRC provided feedback and direction to Intel regarding development of the DELTA system. Improved global sum algorithms, developed by MSRC staff to further MSRC applications, were also incorporated into the standard DELTA system software and are being licensed to Intel for incorporation in commercial products.

The communication system performance of the DELTA computer was examined in detail and compared to that of the iPSC/860. Significant qualitative differences were found, and it became apparent that performance metrics commonly used in the literature were not sufficient to accurately characterize these two machines. New measurement methods and metrics were developed, validated, and disseminated. These findings are described in more detail in a subsequent section on parallel communication system performance.

Parallel Computation Kernels

One kernel that has been studied is the eigensolution of dense real symmetric matrices. Many electronic structure calculations require finding the eigenvalues and eigenvectors of matrices having size N of a few hundred. When these calculations are performed on a large-scale parallel computer, the number of available processors P may be comparable to N . Performance in this regime is not well understood. Prior studies of parallel linear algebra, including eigensolvers, have concentrated on the case $P \ll N$, where it is relatively easy to get good parallel performance by using uniform data distributions to parallelize a conventional sequential algorithm. However, when P is comparable to N (the "large- P regime"), the effects of load imbalance and communications cost become more complicated, and significant performance improvements can be obtained by using nonuniform distributions.

In previous years, MSRC studies had concentrated on full solutions (all eigenvalues and eigenvectors) of small dense matrices, using Jacobi and QR methods. In 1992, the study was expanded to include the "bisection plus inverse iteration" method and to include partial solution (some but not all eigenvectors) of larger matrices ($N < 5000$). In earlier work, inverse iteration methods had been developed that were highly parallel or highly accurate, but not both—the refinements that produced high accuracy tended to reduce parallelism. For certain kinds of matrices, the algorithms reverted to sequential behavior. In collaboration with Dr. Elizabeth Jessup of the University of Colorado, we developed and validated a new inverse iteration procedure that is both highly accurate and highly parallel, producing good speed-ups even for difficult matrices (Figure 1.1). This algorithm is currently being incorporated into the FLAPW code, a prototype augmented plane wave electronic structure program.

Studies continued on the global vector sum problem. This task, defined as adding together vectors contained in all processors of a parallel computer system, is a demonstrated bottleneck for molecular dynamics calculations using the replicated data strategy. In collaboration with Dr. Robert van de Geijn of the University of Texas, we have implemented and analyzed the behavior of several algorithms appropriate for mesh topology machines like the DELTA. Some of these algorithms are uniformly superior to those developed in previous years, and have replaced them. However, the current work continues to show that different algorithms are appropriate in different regimes (i.e., with different vector lengths and numbers of processors). For the DELTA system, no fewer than three completely different algorithms have been found, each of which is superior by a factor of at least 1.5 in some regimes (Figure 1.2). For mid-length vectors ($N=5000$), a new algorithm developed by MSRC staff is up to three times faster than those used previously. This code was introduced into an EMSL molecular dynamics program, and resulted in a twofold increase in overall performance.

Parallel Communication System Performance

To support performance modeling of the computational kernels, a study was performed of the communication system performance of the iPSC/860 computer and the DELTA computer. This study was designed to characterize performance for application programs that have the potential to overlap operations, such as

Figure 1.1 Parallel performance (speedup) of an improved inverse iteration procedure for solving eigen problem.

Figure 1.2. Observed performance of 6 algorithms for global vector sum on the Intel Delta supercomputer (512 processors). Note that halving, exchange, and their hybrid can be used only with $2n$ processors; the other algorithms work with arbitrary numbers of processors.

simultaneously computing, receiving, and sending. It was found that these two apparently similar machines have qualitatively different characteristics. While the DELTA communication channels are faster, they also require much more attention by the application processor, which effectively prevents overlapping most operations. The overall effect is that the DELTA is less powerful for some applications than would be expected based on simple benchmark statistics. Benchmark programs were developed to quantify these effects, and further collaboration is planned with the vendor to develop improved support for this type of application.

2. Graphics and Visualization

E. N. Thornton and D. R. Jones

Computer graphics continue to provide insight to the scientific community. Our computer graphics efforts focus on identifying and developing scientific visualization tools to help address the challenge of the EMSL to model "Molecular Processes in Natural and Contaminated Environments."

In January 1992, a suite of Advanced Visualization System (AVS) modules were combined to form SPACE 1.0. This AVS application was specifically developed to further the study of crystalline structures at the EMSL. As a prototype package, SPACE has helped and continues to help determine the level of effort required to bring visualization tools to the desktops of scientists. Development is progressing with close collaboration from scientists within the MSRC Theory, Modeling, and Simulation program. This close collaboration allows for flexible software design and ensures that the implementation is appropriate.

The AVS was chosen because of its flexibility and extensibility, and most importantly, it was available when the prototyping effort began. The AVS is a general purpose visualization system that provides the capability to apply some of our solutions to other problems in the future. The AVS also allows us to maintain the scientific code independent of the graphics system. The AVS facilitates access to a large existing visualization library, which can be seamlessly integrated with our own in-house software. A final advantage is that the AVS is available on most major UNIX-based computers.

SPACE 1.0 assists scientists in two main tasks. The first is to view crystal models, and the second is to view the results of calculations on crystals.

For viewing crystal models, SPACE allows the simple Ball and Stick displays. It can also generate the unit cell of a crystal, given an asymmetric unit and a space group number for that crystal. The lattice of a crystal may be displayed along with the crystal itself. Another useful feature of SPACE is the ability to interact with displayed objects. Distance, location, angle, and torsion between atoms can quickly and easily be determined by pointing and clicking with the mouse unit on the computer.

For viewing the results of calculations on crystals, SPACE allows automatic input of CRYSTAL output

files. So, for example, electrostatic potentials from a CRYSTAL calculation may be read into a SPACE AVS network and visualized with minimal effort or data transfer. Several methods for two- and three-dimensional data visualization were developed including creation of isosurfaces from volumetric data sets.

SPACE 1.0 was presented to the First International AVS Users Group Meeting in February 1992 and at the DOE Computer Graphics Forum in May 1992. The SPACE software is available on SGI, SUN, DEC, and IBM UNIX environments.

Currently we are working on version 2.0 of SPACE. This version provides the ability to visualize and solve additional crystallographic problems. The features of this software are outlined on page 92 of this report in the subsection entitled Graphics and Visualization of Crystals.

We are also currently working on improving the code development cycle for scientific visualization software. Portability between various UNIX environments is being improved by use of the Andrew File System (AFS). New visualization products are being evaluated, such as IBM's Data Explorer and SGI's Explorer. Other object-oriented development environments are also being reviewed. We are confident that by seeking better portability, better visualization tools, and better development environments, visualization code development in the EMSL will be completed more efficiently and provide a product that is valuable to the scientist.

3. Distributed Computing

**J. O. Schroeder, T. A. Harper, and
T. J. Mathieu**

Providing network-based computing services to desktop workstations is the purpose of the MSRC distributed computing activity. These services include file and software management, backup, printing, mail and messaging, and name services. Currently, distributed computing services are being provided to approximately 125 MSRC staff using a network of about 70 UNIX workstations and servers and about 100 Macintosh computers.

Notable improvements were made this year in the areas of UNIX distributed file services and software

license and Macintosh system management. These items are discussed in the following subsections.

Distributed File Services

The investigation of distributed file systems technology started last year with the acquisition of the AFS software from Transarc, Inc. Following a favorable evaluation in the Distributed Systems Laboratory, the software was moved early this year into limited production use in the MSRC. Three file servers were established on the network, supporting approximately 20 client workstations.

Having established AFS performance as at least equal to SUN's Network File System (NFS), attention has been directed this year to integrating AFS into the production computing environment. The sizing and management of file volumes is critical to successful use of AFS, and some experimentation was necessary to establish policy and parameters that work in the MSRC. Backup policy and procedures have been set up, and shared files and user accounts are being moved from established NFS servers to AFS servers. User documentation has been prepared, describing the structure of the file system, operating procedures, and policy.

The AFS uses a client disk caching scheme that reduces network traffic and speeds access to commonly used files stored in the client's disk cache. Critical file sets can be replicated on multiple servers; if a server fails, the AFS automatically redirects clients to an alternate server. These and other performance/reliability features of the AFS will enable MSRC workstations to operate in a "dataless" mode where user files, shared software, and selected operating system files are stored on the servers.

Distributed file services are critical to the MSRC computing environment. When the AFS is fully implemented, management and operation of MSRC computing resources will be greatly simplified. For example, the servers will be a focal point for backup of all user files. Users will see a consistent view of the file system and be able to access their home directories from any workstation on the network. Administrators will maintain a single copy of shared software, rather than replicating changes to individual workstations.

The AFS software is now operational on SUN, DEC, IBM, and HP clients in the MSRC. Transarc, Inc.,

is seriously considering porting AFS to SGI clients. When Transarc's SGI client software and Macintosh client software (being developed by the University of Michigan) is installed, all strategic computing environments in MSRC will be supported by the AFS.

Software License Management

The KeyServer software license manager developed by Sassafras Software, Inc., was made operational on the MSRC network this year. Through KeyServer, MSRC Macintosh users have access to a wide range of applications software. Software acquisition and management costs are greatly reduced, and users have immediate access to new and updated applications. Installation of new systems is especially convenient since Macintosh applications software is managed on an MSRC-wide basis rather than for individual machines.

When a user launches an application that has been "keyed," a software key is checked out from a pool managed by KeyServer for as long as the application is in use. If all the available keys for a particular application are checked out, users requesting the application are queued on a first-in first-out basis. The key count is set to the number of licenses that have been purchased. Access to selected applications can be restricted or prioritized for use by selected users or groups, or made available to all users.

KeyServer is now being used by several MSRC groups to manage all of their application software, including specialty applications that are not commonly used and mainline applications such as word processors. Specialty applications can be expensive and KeyServer has proven effective at reducing this cost. For example, the upgrade to Excel 4.0 for 80 MSRC staff members costs \$1800 rather than \$8000 for individual upgrades.

Macintosh System Management

In addition to the Keyserver service, several other facilities have been or are being implemented to facilitate management of the Macintosh systems. Network Supervisor has been deployed to enable support staff to remotely access customer systems for status information and to accomplish certain corrective actions without leaving the office, which has made them more productive.

Network Distributor, which works in conjunction with Supervisor, enables support staff to deliver software to remote systems, again from their own offices. Automated procedures have been developed to distribute KeyServer applications to staff requiring them. This facilitates upgrading all software programs to current versions while minimizing interference with the productivity of the scientists, and enabling support staff to be more productive.

The final piece of the Macintosh support model is the remote backup of systems. This service, also dependent on Supervisor, was tested with selected MSRC staff and deployed in the fall of 1992. The staff member can leave the workstation on or shut it down as normal. The backup system will access each system during the night to backup critical files and then complete the system shutdown, if requested. Lost or corrupted files can be recovered within a day or two upon notification to support staff.

The net effect of these improvements has been to make the Macintosh environment consistent across systems with improved reliability and to make more efficient use of support staff time. The result is improved service at reduced cost per system.

4. Computer Interfaces and Electronics Data Acquisition Systems Development

G. A. Anderson, D. W. Arlt, R. T. Kouzes, K. D. Steele, and E. W. Wallace

The Computer Interfaces and Electronics group carried out several development projects in the area of computer-based data acquisition and control hardware and software. This development work was carried out partially in the Interface Development Laboratory (IDL). The IDL, established in 1992, is required for the development and testing of data acquisition and control instruments, electronics, interfaces and software associated with all of the MSRC research programs. The IDL provides the tools and environment to develop instrumentation interfaces, perform instrument modeling and optimization, and research prototype data acquisition and control systems. The IDL and associated staff are

involved in consultation, design, integration, and support roles for the EMSL instrumentation development projects.

A Time Resolved Transient Absorption (TRTA) data system was developed for the Chemical Structure and Dynamics program. This DOS-based application is used to control an optical delay line, to input data from an ADC board within the computer, and to display spectra on the screen. As part of this project, physical interfaces between the experimental apparatus and the computer were fabricated.

A Tandem Time Of Flight (TTOF) mass spectrometer data system was also developed for the Chemical Structure and Dynamics program. This system controls an optical delay line and a tunable dye laser, uses an interface to computer automated measurement and control (CAMAC) instrumentation for data collection, and displays and stores spectral data from the mass spectrometer. A byproduct of this work was a set of software tools for general usage in data acquisition systems.

An experiment controller for neutral ion research included a stepper motor and controller to serve as a chopper for a laser, plus logic to generate the timing signals to trigger the instruments in the experiment. The controller also contained a precision ramp generator used to sweep the laser wavelength.

A data acquisition and control system for a Laser-induced Fluorescence (LiF) experiment has been developed. This provided an opportunity to test Visual Basic software as an environment for some of the MSRC needs in data acquisition. The data rate obtained, about 20Hz, is sufficient for this application and provides a benchmark for future usage.

Several detector concepts were researched and prototype detectors were fabricated and tested for a Tandem Mass Spectrometer (TMS) position sensitive detector. One prototype detector, consisting of a delay line etched on a printed circuit board, is the first of its kind. Overall computer data system architectures for the Theory, Modeling, and Simulation program were also evaluated.

In the area of Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS), all major vendors and leading university laboratories were visited to learn about the latest developments in the field. The IonSpec FTICR-MS system, installed in the MSRC this year, was substantially modified to improve

its sensitivity and noise rejection. Development of improved preamplifiers and a data system have begun. This effort will allow us to evaluate the state-of-the-art in FTICR and better prepare us to design and specify components of the planned 12-Tesla system. A new ICR cell design has been constructed as an upgrade for the IonSpec system and to allow evaluation of improved cell designs for future systems.

Neural Network Applications

L. J. Kangas and R. T. Kouzes

Artificial Neural Networks (ANNs) are likely to play a role in the EMSL project in applications to data acquisition and analysis. One of the tasks is to evaluate how ANNs might be used in the project, and to perform prototype implementations. There are two goals to this evaluation; one specific and one general.

The first goal is to perform an investigation of software and hardware back-propagation (and other) ANNs with applications to sensor array data acquisition and analysis. The ANNs will play a role in the data acquisition for sensor arrays developed within the MSRC requiring prototype development. The application is to real-time processing of data from multisensor arrays that provide overlapping response to a chemical environment. Prototype evaluation of ANN data acquisition will be carried out with software simulation, then with software implementation with sensor arrays, and finally with ANN hardware, if the prototyping gives positive results.

The second goal is to evaluate other potential applications of ANN technologies to EMSL projects. The ANNs have been applied to a number of problems that might have direct application to analysis problems arising in the EMSL project, such as spectral analysis, categorization of objects based on multi-parameter data, and data compression. We must make an evaluation of these possible applications, and pursue the most promising of them for the MSRC programs.

The first step in the application of ANNs to the project is to prepare an evaluation of the approaches to these two goals. The result of this study is a report defining options for how neural network software and hardware can be used to solve the data acquisition problems for multisensor arrays, and outlining specific recommendations on how neural networks can be used to solve a variety of analysis problems in the EMSL project.

An investigation has been initiated to identify the specific problems where ANNs may be the preferred solution and to match the ANN technology with major applications already identified or expected within the EMSL project. Identification of these applications is performed by expert scientists already involved in developing applications, and by research of literature describing ANN solutions to applications that might be found in the project.

Several possible applications for ANN technology have been identified for the Theory, Modeling, and Simulation program in determining molecular structures from NMR spectroscopy, mass spectroscopy, and infrared spectroscopy. The program work also includes determining how amino acids in proteins fold, determining the rotations of amino acids in protein chains, and solving optimization problems. For example, molecular structures can be determined by computing the energy minima and equilibria of their subcomponents. These problems are nonpolynomial (NP)-complete and thus have no algorithmic solution. Genetic algorithms (GA), like ANNs, are biological models that efficiently find good solutions to these types of search and optimization problems.

Another possible application for ANNs is data compression of histograms. The Chemical Structure and Dynamics program is developing methods for performing photon counting of fluorescent molecules where the histograms are two-dimensional maps of a surface. The initial size of one of these histograms is a 1024 by 1024 square of 16-bit elements (counts). The storage requirement of one uncompressed histogram is 2 MB. The desired histogram size after the initial development is 2048 by 2048, which requires 8 MB of storage, and the use of even larger histograms may become necessary in the future. Data compression compresses the histogram data so that it requires much less storage memory in the computer. Although some information loss occurs, the nature of the data in the histograms suggest that a very large data compression would only result in a minimal data loss. A recognized approach in data compression of this form is to tile the histogram into squares, e.g., 64 by 64 elements and then compress each individual tile using Principal Component Analysis (PCA). The ANNs can be trained in either hardware or software to perform efficient PCA data compression in real time. The staff from the Chemical Structure and Dynamics program has also suggested that data compression of spectroscopic data is desired.

The Computing and Information Sciences program provides processing and storage capabilities for scientific data in the MSRC, including data in the form of numeric results and in images. The need for data compression will become evident since data storage and communication networks are valuable resources that will deplete with the increase of data. Data compression should be considered as a cost-effective means to remedy this problem. Data compression can be divided into two types: with or without data loss. Commercial software is available to compress data without loss. The ANNs are currently used efficiently for data compression where some data loss is acceptable. One such recognized method for data compression is by using ANNs to perform PCA as a means of reducing data into lesser dimensions. This inevitably results in some data loss. Therefore, all data that need to be stored should be analyzed to determine the degree of acceptable data loss to determine the applicable compression method.

An objective of the MSRC Materials and Interfaces program is to develop new chemical sensing methods. This includes both designing new sensors and finding new methods for analyzing the data collected by these sensors. During discussions with this group, several applications were identified for use of ANNs: multi-sensor array analysis, sensor calibration, sensor validation, data compression, and process control. The Molecular and Interfaces program has identified the need for a sensor composed of an array of eight elements, with each of these elements measuring different properties of the sensed chemical. These elements also measure different chemical properties at different temperatures and thus a matrix of data is collected by varying the temperature of the chemical during sensing. This matrix of data, with a dimension of eight by the number of sensed temperatures, is analyzed to determine the chemical structure. The complexity of the data collected by this sensor makes it difficult to use conventional analytical methods. The ANNs, which are relatively easy to program for analyzing complex data, are being considered for the sensor data analysis. The development of new sensors requires the establishment of a methodology for sensor calibration and validation. This involves the identification of tested methods and the development of new methods. The ANNs should be considered for both the calibration and validation of new sensors, particularly for new complex sensors, on which they may perform better than established calibration and validation methods.

The MSRC will be involved in the cleanup of the Hanford Site. This work will require that exact chemical process controls are in place. The ANNs have successfully been used in the control of complex processes in the past and should therefore be considered in the control needs in the EMSL project.

Modeling and Simulation

R. T. Kouzes

Part of the development process for state-of-the-art instruments requires modeling the performance of the instrument under varying design parameters to optimize the response of the instrument. The Computer Interfaces and Electronics group research program in instrumentation includes computer modeling and simulation of the physics applicable to instruments, the simulation of instrument characteristics, the simulation of data acquisition system response and the simulation and testing of new technologies relevant to instruments.

Ion injection, ion motion and device sensitivity of an FTICR-MS, NMR probe design simulation, and TMS detector performance are examples of device characteristics that can be optimized through computer modeling. The electric and magnetic fields that affect the motion of an ion can be adjusted in simulation to improve the signal to noise, linearity, or efficiency of an instrument. Such simulations are also a valuable learning tool for the experimentalist who is trying to understand an instrument's performance. A good example of this capability is the need to model the magnetic fields for designing the 23.5-Tesla NMR magnet and shield and the 12-Tesla ICR magnet and shield. Calculations of the detailed shape of the magnetic field in the ICR and TMS, and of the electric field in ICR cells are also needed for ion motion studies to improve FTICR-MS performance.

The POISSON family of codes from Los Alamos National Laboratory are extensively used in magnet design for performing two-dimensional electrostatic and magnetostatic modeling. We have used POISSON to model the magnetic fields in two dimensions from the ICR and NMR magnets, including the iron shields to determine the basic requirements for the shield.

The UHF-NMR being designed for the EMSL project will use a 23.5-Tesla superconducting magnet. To bring the fringe field from this magnet down to the 5-gauss level required by safety considerations, an

iron magnetic shield room for the magnet is planned. The POISSON code was used to determine what shield thickness is required. This code, running locally on a SUN workstation, takes a description of the geometry and processes it through four steps to determine the magnetic field. The magnet geometry was assumed to be a series of cylindrical coils, which is an approximation to the NMR magnet design producing a magnet with a stored energy of 27 Mega Joules. The basic conclusion is that at least 4.3 cm of 1006 steel are required to bring the field down to the 5 gauss level outside the 3.8-meter radius cylindrical shield. Figure 4.1 shows the result of one calculation.

Electromagnetic Noise Measurements at PNL

G. A. Anderson, R. T. Kouzes, J. M. Larkin, and E. W. Wallace

Electromagnetic noise is a general problem in all laboratory environments. In designing a new laboratory that will house a wide variety of instrumentation, it is useful to have some understanding of

Figure 4.1. The magnetic field lines in one quadrant for a solenoid magnet (lower left) in a cylindrical steel room. This illustrates how the field is constrained to follow the steel walls.

electromagnetic noise sources and ambient background levels in a typical research space that can be used as a base-line for shielding requirements. Our staff have made a series of measurements of the electromagnetic spectrum using calibrated instruments as part of the planning process for construction of the EMSL building.

The EMSL will house a range of equipment, including FTICR-MS, NMR, TOF-MS, pulsed laser-induced fluorescence, and scanning microscopy instruments. There will also be a large number of computers in the EMSL, including high-performance and parallel computer systems. This mix of equipment produces a noisy electromagnetic environment that is detrimental to some of the sensitive instrumentation, requiring the design of shielded rooms in the facility. Measurements were made in existing laboratory spaces at PNL to gain a knowledge of the ambient electromagnetic spectrum in typical laboratory spaces.

Measurements were made of the electromagnetic spectrum from 10 kHz to 1.5 GHz at various sites around PNL. The electric field strength measurements were carried out using a spectrum analyzer and a set of calibrated antennas. Measurements were taken using an HP 8590A Spectrum Analyzer connected to a passive monopole antenna, an adjustable dipole antenna, and a double-ridged guide antenna.

Readings from the spectrum analyzer were in dBmV. Photographs were taken of the spectrum analyzer display, one for each of the various antenna configurations and orientations per site. Peaks in the electromagnetic field were found from these photographs and their frequency in MHz and strength in dBmV were recorded. Values of dBmV/m were calculated by adding an antenna factor and coaxial attenuation loss to the peak value in dBmV. The electromagnetic peak data was then plotted for each of the test sites using the Physics Analysis Workstation (PAW) code from the Center for European Nuclear Research (CERN). Baselines reflecting the minimum signal that could be distinguished for each of the antenna configuration were added to each of the plots.

Several of the plots contain broad spectral peaks in electromagnetic noise that could not be distinguished into individual peaks at specific frequencies. The strongest electromagnetic fields measured at the EMSL site were due to local AM, FM, and television broadcasting. The signals from AM, FM, and television stations were reduced inside buildings, especially in basements and the central areas of the buildings.

The spectra are characterized by a number of lines arising from local radio and television stations, cellular phones, and CB and short wave radio sources. Some lines can be attributed to specific instruments such as a 300 MHz line from the NMR instrument. The line sources measured have an intensity as great as 65 mV/m, and broad structures at the several mV/m level were observed. These lines are on top of a broad electromagnetic baseline that varies greatly with location. The baseline levels observed were as low as a few $\mu\text{V/m}$, but levels of a few hundred $\mu\text{V/m}$ were measured at some sites.

The measurements from the various test sites revealed that much of the electromagnetic noise indoors is found below 10 MHz. Of most concern was the noise below 3 MHz. Several of the most sensitive instruments in the laboratory obtain data in this region and will be adversely affected by excessive electromagnetic noise at these frequencies. Most locations where measurements were made show similar electromagnetic noise levels, with a few unique lines or broad features occurring near certain instruments. A characteristic of most of the spectra is the almost white noise nature of the radio frequency (RF) observed at the level of tens of $\mu\text{V/m}$.

These results provide a baseline reference for the shielded room specifications, and provide input to the design for the EMSL building. This data can allow for a more detailed specification of the frequency dependence of the required instrument shielding. (Figure 4.2)

5. Scientific Networking

**M. J. Peterson, T. A. Harper, and
K. D. Steele**

Distributed, high-performance scientific computing places challenging demands on current network technologies and commonly practiced network design techniques. Most commercially available network products and technologies are suited to predictable business environments of batch processing, file transfers, electronic mail, and printing. The MSRC scientific and theoretical research has the requirement for moving large data sets among different computing architectures varying from very high-performance workstations on the desktop to massively parallel highly computational intensive resources. Other challenges include applications that are distributed

Figure 4.2. Typical spectrum in log-log format showing spectral features observed, and the position of radio and television bands compared to the EMSL site electromagnetic spectrum.

throughout the facility using idle desktop resources in a loosely coupled parallel processing mode.

Network prototyping in the past year has focused on tasks supporting the design of the EMSL, and on understanding the network requirements of the molecular scientist. Progress has been made in obtaining space and resources to create a Distributed Test and Evaluation Lab (DTEL), which is used in conjunction with the Distributed Computing System task. This test environment has gathered computing resources to emulate workstations and servers as well as obtain the necessary software to characterize and measure network performance.

The DTEL has the necessary equipment to easily emulate many network architectures for evaluation. Several Fiber Distributed Data Interface (FDDI) networks can be connected through multiprotocol routers to individual Ethernet subnetworks. Network analyzers for FDDI and Ethernet can be called upon to measure network traffic, trap data packets, and to provide background network loading to test near

real-world scenarios. Once a network concept has been fully tested in the controlled lab environment, it is then placed into service for further testing and evaluation by scientists running real applications.

The network prototyping also supports early development efforts for other tasks within EMSL. This modular prototyping of the related tasks allows systems to be quickly developed and intelligently scaled as requirements evolve. Other tasks that the network will support include distributed computing systems, high-performance computer system, database computer system, graphics and visualization laboratory, molecular science software development, and MSCF software development.

The goals for the EMSL network are to provide high-performance, reliable, and easily reconfigurable networks supporting the special experiments and computational intensive processes that will occur in the EMSL. This will be accomplished by designing and installing multiple, partitioned networks to serve fewer users (10-25) than is currently practiced (100s) in classic network design. Users will be grouped logically as well as physically on networks, minimizing contention for bandwidth. Critical or often accessed resources will be directly connected or tightly coupled to user's local networks. This close coupling will be accomplished while maintaining centralized management of network systems.

Not all classes of computers require higher cost gigabit performance networks. Consequently, EMSL networks have been broadly categorized into three areas. Each of these classes of service have tradeoffs between performance, reliability, cost, manageability, and maturity/availability of products that can meet requirements. Reliability is very critical for the End-user Subscriber Networks (ESN) and Backbone Information Networks (BIN), as office resources will be dependent on maintaining links to other computer resources in the EMSL. The three classes of networks will be interconnected and are envisioned to be designed into a hierarchical relationship to match the performance needs of the computer resources that are attached. The highest performance network is the Computer-to-Computer Network (C2N), which will serve the transmission needs of the high-performance systems in the EMSL. The classes of network performance criteria are summarized and briefly discussed below:

Criteria	Class of Network	Target Range
Speed/Throughput	ESN	10-100 Mbits/sec
	BIN	100-200 Mbits/sec
	C2N	500-1000 Mbits/sec
Packet Sizes	ESN	60-1500 Bytes
	BIN	1500-4000 Bytes
	C2N	>4000 Bytes
Unplanned Outages	ESN	<0.1%/yr (9hrs/yr)
	BIN	<0.2%/yr (18hrs/yr)
	C2N	<0.5%/yr (44hrs/yr)

The ESNs, if implemented with today's technologies, would be Ethernet over twisted pair wiring or fiber optics. By 1994, when the network cabling is scheduled to be installed, higher speed FDDI class networks will be widely used and will possibly replace Ethernet as the common desktop network. High-end workstations in offices will require bandwidths higher than FDDI and transmission needs cannot be met with twisted pair copper media. Because of this, fiber optics was selected as the preferred media for the EMSL during the Title I design. By using fiber optics instead of copper, the potential bandwidth to the desktop is not constrained by the cable plant.

If implemented today, ESN subnets could be interconnected over the BIN with high-performance routers to multiple-ring FDDI networks. Local subnets would access high-speed resources and servers on a local FDDI subnet ring, and remote resources could be accessed through the multiple ring FDDI backbone. Figure 5.1 depicts this network architecture as envisioned using technologies available today. It is important to note that the facility cabling has been designed in such a manner that topology changes, reassignment of users to physical networks, and reconfigurations can be accomplished without changes to the cabling system. Through easily reconfigurable patch panels, the entire facility cabling scheme can be changed almost overnight.

The C2N network class has the least number of product choices available for its implementation and is the most complex. Technology is changing very rapidly in this area, and the selection of candidates can have a large impact on the type of wiring chosen (fiber optics, coax, or multi-pair copper), topology (ring, star, point-to-point), and overall architecture. Distance limitations affect placement of high-speed computer resources,

Figure 5.1. ESN/BIN Network Architecture

data archive resources, high-performance graphics workstations, computer servers, and laboratory computers. Experience gained in prototyping will directly drive the Architect and Engineer (AE) network design for the facility, as well as selection of candidate technologies for implementation in the EMSL. Technologies being evaluated include High-Performance Parallel Interconnect (HiPPI), asynchronous transfer mode (ATM), Fibre Channel, and others.

Extensive tests will be performed in the next year on various network architectures in support of the ESNs and BIN networks. Requirements and technology assessments will be performed on the C2N prototyping, with plans to have a system in which to test later in the year. Efforts will focus on gaining performance data that will allow us to design and implement a fully functional network in support of the computational-intensive applications that will exist in the EMSL. The challenges that lie ahead can have a positive effect on the ease with which scientists can apply computational resources to solving complex molecular research in search of new ways to clean up our environment.

Appendix

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Appendix A

MSRC Staff and Associates

Appendix A

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MSRC Management

Dr. Michael L. Knotek is Manager of the MSRC and the EMSL, and the Senior Director, Science and Technology, for PNL. From 1985 to 1989, Knotek chaired the National Synchrotron Light Source, a DOE user facility located at Brookhaven National Laboratory. Before joining PNL, Knotek was affiliated with Sandia National Laboratories; the Naval Weapons Centers at Corona and China Lake, California; and Ames Laboratory at Iowa State University. In 1984, Knotek was recognized by the DOE Office of Basic Energy Sciences for outstanding research in solid-state physics for his work on stimulated desorption. In 1985, DOE recognized him for outstanding scientific accomplishments in metallurgy and ceramics for work on stress corrosion cracking in solids. In 1987, he became a Fellow of the American Physical Society.

Knotek earned his Ph.D. in physics at the University of California-Riverside in 1972. He was also a Visiting Scholar at the Cavendish Laboratory, Cambridge University, England. He worked on the Quantum Theory Project at the University of Florida and on transport in organic systems at Oklahoma State University. Knotek is a member of Sigma Xi, the American Vacuum Society, the American Physical Society, the American Chemical Society, and the American Association for the Advancement of Science.

Knotek was co-chair of the planning study for advanced national synchrotron radiation facilities. He is currently chair of the Proposal Evaluation Board for the Advanced Photon Source at Argonne National Laboratory. He also is a member of the Program Review Panel for the Advanced Light Source at Lawrence Berkeley Laboratory, the Stanford Synchrotron Radiation Laboratory Review Committee, the University of Texas at Austin Science and Technology Advisory Committee, and the American Physical Society Panel on Public Affairs and the Division of Condensed Matter Physics Strategic Planning Committee. He serves on the board of directors of the Idaho Research Foundation, Inc., and the Washington Technology Centers. He has

more than 80 publications on topics ranging from theories of charge transport to the effect of radiation on chemical bonding.

Dr. B. Ray Stults is the MSRC Deputy Manager for Programs and program manager for the BES-Chemical Sciences research programs at PNL. Previously, Stults was the manager of PNL's Chemical Sciences Department. Before joining PNL, Stults was an Associate Science Fellow at the Monsanto Company where he supervised research programs in small-molecule, x-ray crystallography; powder diffraction; x-ray adsorption spectroscopy; and surface science.

While with Monsanto, Stults developed an expanded program in surface science, including x-ray photoelectron spectroscopy, secondary-ion mass spectroscopy, and Auger spectroscopy. In addition, he developed a laboratory for protein engineering that included protein x-ray crystallography, interactive molecular modeling, and macromolecular dynamics simulations.

Stults is a member of the American Chemical Society, the American Crystallographic Association, Sigma Xi, Phi Lambda Upsilon, the American Society for the Advancement of Science, and the Materials Research Society. He received his Ph.D. in inorganic chemistry from the University of Nebraska and did postdoctoral research with Professor F. A. Cotton at Texas A&M University. He has written more than 50 papers in the areas of crystallography and structure/function analysis for systems ranging from homogeneous catalysts to organic compounds active as agricultural products.

Dr. M. Tom Thomas is the MSRC Deputy Manager for Science Integration and Implementation. He is responsible for ensuring that the EMSL Project technical scope integrates fully with the MSRC and other PNL Research Centers. Also, he is responsible for establishing the appropriate protocols so the EMSL can be used as a collaborative research facility. In addition, he oversees and manages all aspects of operations for the interim MSRC/EMSL facilities,

including Environmental Safety and Health, National Environmental Policy Act, property, and space allocation. Previously, Thomas was Manager of the EMSL Project during the planning, conceptual design, and initial start-up phases. Prior to that, he was Manager of Research Operations and Services for the MSRC. Before assuming managerial duties, Thomas was a Staff Scientist and Group Leader responsible for developing an applied surface science group and a surface science analytical facility for PNL. His general research interest is in applying surface science to solve materials problems associated with surface and interface phenomena.

Thomas's research experience includes a study of environmental effects on fracture, grain boundary chemistry, and stress corrosion; material degradation due to corrosion; and wear and tribology. He also is developing standards for surface analytical studies (AES, XPS, SIMS, etc.).

Thomas has conducted research on problems related to industrial surface/interfaces, interfaces in mineral processing, and silicon/gold interfaces as well as surface problems in fusion technology, including first-wall neutron sputtering and plasma/wall interactions in Tokamak plasma machines.

Thomas is immediate past chairman of Committee E42 on Surface Analysis of the American Society for Testing and Materials and is a member of the American Vacuum Society, the American Institute of Mechanical Engineers, the American Physical Society, and the American Association for the Advancement of Science. He has been appointed the U.S. Delegate to the International Organization for Standardization's (ISO) Technical Committee 201 on Surface Chemical Analysis and is serving as chairman of the U.S. Technical Advisory Group for ISO/TC 201. During the past year he was also appointed U.S. Delegate to ISO/TC 202 on Microbeam Analysis and is a member of the Technical Advisory Group for ISO/TC 202. He received his Ph.D. in solid-state physics/surface physics from Brown University.

Thomas has written more than 50 papers on material science studies in energy technologies involving passivation and corrosion of amorphous materials, effects of grain boundary chemistry on stress corrosion, corrosion of iron alloys, and neutron sputtering from candidate fusion reactor first-wall materials. In addition, he has published review papers on the application of surface science techniques to study problems in tribology, mineral processing, and applications of surface analyses.

EMSL Project Management

Dr. James K. McClusky is Manager of the EMSL Project. McClusky has 29 years of experience in the nuclear and chemical processing fields, with 20 years in project and program management.

Prior to joining Battelle in 1991, McClusky was a Director at EG&G's Rocky Flats Plant. From 1977-1988, he held a number of responsible management positions with Rockwell International at Hanford. In 1983, McClusky led the successful restart of the Purex Chemical Processing Plant for Rockwell.

McClusky received his Ph.D. in nuclear/chemical engineering from Iowa State University in 1971. He was awarded a Post-Doctoral Fellowship at Ames Laboratory during 1972.

McClusky holds several patents in the area of nuclear fuel preparation. He is a member of the American Nuclear Society and the American Institute of Chemical Engineers.

Chemical Structure and Dynamics

Dr. Steven D. Colson became Associate Director for the MSRC Chemical Structure and Dynamics program in 1989. Between 1968 and 1989, Colson progressed from Assistant Professor to Professor of Chemistry at Yale University. Colson has written or contributed to more than 100 papers on photochemistry, photophysics, and molecular dynamics; electronic structure of molecules, radicals, and molecular ions; processes at the molecule/surface interface; and intermolecular interactions in molecular solids.

In 1984, Colson was chairman for the Gordon Conference on Visible/UV Multiphoton Ionization and Dissociation Processes. He was also chairman of the 21st International Symposium on Free Radicals in 1991. From 1985 to 1987, he was a member of the Petroleum Research Fund Advisory Board. In 1988, he was guest professor at the University of Ulm in West Germany. He has also served as Associate Editor of the *Journal of Chemical Physics*. Since joining the MSRC, Colson has been appointed an Affiliate Professor in the Chemistry Department at the University of Washington and an Adjunct Professor of Chemistry at Washington State University.

Colson received his Ph.D. in chemistry from California Institute of Technology in 1968 and spent a year as a Postdoctoral Fellow at the National Research Council

in Ottawa, Canada before moving to Yale. He is a member of the American Chemical Society. Recently, Colson was awarded a Humboldt Fellowship by the Alexander von Humboldt Foundation in Germany. This award, which was in recognition of his past accomplishments in research and teaching, allowed Colson to study for six months at the Institute for Physical and Theoretical Chemistry in Munich.

Dr. Stephan E. Barlow recently joined the Chemical Structure and Dynamics program as a Senior Research Scientist. He received his Ph.D. in chemical physics from the University of Colorado at Boulder in 1984, working on very-low-temperature ion trapping techniques under the guidance of Professor Gordon H. Dunn of the Joint Institute for Laboratory Astrophysics (JILA) and the National Institute of Standards and Technology (NIST). He was a postdoctoral fellow in the Chemistry Department of the University of Colorado with Professor Charles DePuy and Dr. Veronica Bierbaum. Most recently he was an instructor in the Chemistry Department at the University of Colorado, Denver.

Barlow's work with ion traps led to techniques that allowed gas-phase, ion-molecule reaction kinetics to be studied at temperatures below 77 K for the first time. His work in Professor DePuy's laboratory led to the development of greatly improved Selected Ion Flow Tube technology. Most recently he has been investigating the nature of clusters and cluster formation, work that will be continuing at the MSRC with new instrumentation.

Barlow's ion-trap work has also led to an interest in the physics of charged-particle storage. He was one of the first to apply the theory of non-neutral plasmas to the behavior of trapped ions. He is using such concepts to develop improved mass spectrometric techniques.

Dr. James P. Cowin is a Senior Research Scientist in the Chemical Structure and Dynamics program. His experimental research program looks at molecular dynamics of molecules adsorbed on surfaces, light-stimulated surface reactions, and charge transfer processes. His work includes making well-characterized models of the water/solid interface, complex multilayer structures, and single molecule photochemistry with the scanning tunneling microscope. He is the author of more than 30 papers. Before coming to PNL, Cowin was an Assistant Professor of Physical Chemistry at the University of California-Santa Barbara,

where he was recognized as one of the pioneers of laser-driven surface reactions. He studied chlorinated and other halogenated hydrocarbon surface chemistry. He maintains a collaboration and membership there in the Quantized Electronic Structures Group.

Cowin earned his Ph.D. in chemistry at the University of Chicago in 1981 under the direction of Professor Lennard Wharton and built one of the first universal molecular-beam surface machines. His studies included many aspects of surface energy transfer and structure, most notably the first quantitative use of laser surface heating for kinetic studies and the discovery of the phenomena of rotationally mediated selective adsorption.

Cowin did postdoctoral studies with Dr. John Polanyi at the University of Toronto. He built a beam surface machine and introduced Dr. Polanyi to laser-surface chemistry, now Polanyi's major thrust.

Dr. Donald M. Friedrich, a Senior Research Scientist, is responsible for the experimental study of dynamics at solid/liquid interfaces using the time-resolved and Raman laser spectroscopy capabilities in the MSRC. His previous research in PNL's Materials Science Department involved Raman spectroscopic studies of phosphazene polymers and optical thin-film materials.

Prior to joining PNL, Friedrich was Associate Professor of Chemistry at Hope College, where he constructed a laser spectroscopy laboratory dedicated to undergraduate chemistry research. While on sabbatical leave at the University of Minnesota and the University of California-Berkeley, Friedrich used picosecond and resonance Raman methods to study the kinetics and structural changes occurring during excited-state intramolecular proton transfer in solutions. Friedrich's postdoctoral research at Wayne State University resulted in the first measurement of the polarized two-photon excitation spectrum of benzene. The unexpected nature of the polarization characteristics of this spectrum led to a reassignment of the excited-state vibrations in benzene and a new understanding of vibronic coupling in aromatic molecules.

Friedrich obtained his Ph.D. in chemistry from Cornell University under the direction of Professor Andreas Albrecht. He has written more than 20 publications on the spectroscopy of π -conjugated compounds and free-radicals, inorganic polymers, and thin-film optical materials.

Dr. Wayne P. Hess joined the MSRC's Chemical Structure and Dynamics program as a Senior Research Scientist in 1990. Previously, he was a Postdoctoral Research Associate at the Combustion Research Facility, Sandia National Laboratories, Livermore, California. The thrust of his postdoctoral work involved using cw-LIF to determine precise kinetic rate constants and radical reaction mechanisms. He also studied dissociation dynamics using both LIF and photofragment imaging techniques.

Hess received his Ph.D. in physical chemistry from the University of Colorado in 1988. His graduate studies, conducted under the guidance of Professor Stephen Leone, involved the application of diode lasers to probe photodissociation quantum yields and chemical dynamics. He is a member of the American Chemical Society and the American Physical Society and has written or contributed to over a dozen publications on topics such as photodissociation dynamics, photofragment imaging, radical kinetics, and Raman spectroscopy.

Hess has presented papers at numerous national and international conferences and meetings.

Dr. Gary R. Holtom joined the MSRC in 1989 as a Senior Research Scientist. He is responsible for laboratory operations in the Chemical Structure and Dynamics program, including safety, organization, equipment specification, and user activities. Previously, Holtom was Head of Laser Operations in the Regional Laser and Biotechnology Laboratories at the University of Pennsylvania, where he maintained fast fluorescence techniques at the state of the art, trained local and visiting researchers, and assisted in interpreting results. He also developed apparatus and analysis methods and created software for data collection and analysis.

Holtom's graduate research involved building lasers and associated data acquisition equipment for two-photon spectroscopic measurements using analysis methods originated by his research director, Professor Martin McClain.

As a Postdoctoral Fellow at Connecticut Wesleyan University under Professor Bryan Kohler, Holtom continued his work with high-resolution cryogenic methods. His primary goal was to relate spectroscopic measurements to photochemistry in octatetraene.

Holtom received his Ph.D. in physical chemistry from the University of California-Berkeley in 1978. He has written or contributed to 20 publications on topics ranging from the design of a birefringent filter for high-power dye lasers to time-resolved spectroscopy of the human brain. In addition, he organized and taught a short course in using lasers in chemical research as well as Chautauqua courses on dye lasers and laser methods in chemical research. The latter courses were intended to refresh high school and college teachers in an area of general interest.

Mr. Martin J. Iedema is a Research Scientist in the MSRC's Chemical Structures and Dynamics Program. He joined the program in 1990, working with Dr. James Cowin in research involving the dynamics of molecules adsorbed on surfaces, including photochemical and charge transfer effects. Iedema is also responsible for the MSRC's Scanning Tunneling and Atomic Force Microscopy User Facility, through which a number of collaborations have produced research papers and seminar talks.

Prior to joining PNL, Iedema worked at the Mt. Wilson Observatory with Dr. Ed Rhodes in the field of helioseismology. During that time, he also was a high school science teacher.

Iedema earned his B.S. degree in physics and astronomy from the University of Southern California. He currently is doing graduate work in the Materials Science Department of Washington State University.

Dr. Stephen A. Joyce is a Senior Research Scientist in the Chemical Structure and Dynamics program. He received his Ph.D. in physical chemistry from the Massachusetts Institute of Technology with Professor Jeffrey Steinfeld in 1987, studying reactive processes on silicon and silicon dioxide surfaces. He spent two years as a postdoctoral fellow at the National Institute of Standards and Technology, where he studied stimulated desorption of ions and metastable species from surfaces and conducted the first experiments to measure the angular distributions of negative ion desorption. He was most recently a postdoctoral associate at Sandia National Laboratories, where he developed the interfacial force microscope to directly measure the interactions of two surfaces at nanometer distances to obtain insight into phenomena such as adhesion and friction.

Joyce is interested in experimental studies of atomically-resolved reactions on solid surfaces using scanning probe techniques such as scanning tunneling and atomic force microscopies. He has over 30 publications on surface chemistry and is a member of the American Physical Society and American Vacuum Society.

Dr. Bruce D. Kay is a Senior Chief Scientist in the Chemical Structure and Dynamics program. His main research interests are in the chemical dynamics and kinetics of gas-surface interactions, which he studies using a combination of molecular beam-surface scattering and laser-based spectroscopic techniques. His current research interests focus on the dissociative chemisorption of halogenated hydrocarbons on model oxide surfaces. Prior to joining the MSRC, Kay was a senior member of the technical staff in the Interfacial Chemistry Division at Sandia National Laboratories, Albuquerque, New Mexico. While at Sandia, Kay initiated and was principal investigator on research programs in the areas of quantum-resolved, gas-surface scattering; kinetics of hydrogen in and on solids; gas-phase rotational relaxation; and kinetics of sol-gel formation.

Kay received his Ph.D. in chemical physics from the University of Colorado in 1982. He has written or contributed to more than 60 papers and has presented more than 100 lectures at universities and national and international meetings. He is a member of The American Chemical Society and The American Vacuum Society. In 1991 he received the John Yarwood Medal from the British Vacuum Council for his work in the field of state-to-state inelastic and reactive gas-surface scattering.

Dr. Robin S. McDowell joined the Chemical Structure and Dynamics program in 1991 as Senior Chief Scientist and Program Manager. He received his Ph.D. in physical chemistry from the Massachusetts Institute of Technology Spectroscopy Laboratory in 1961. Most of his professional career was spent at Los Alamos National Laboratory, where he was successively staff member, assistant group leader, and Laboratory Fellow. He has also been associated with the Los Alamos Technology Office at Rocky Flats, where he worked on environmental monitoring and remediation.

McDowell's research interests are in studies of molecular structure and dynamics through vibrational infrared and Raman spectroscopy, employing

Fourier-transform spectrometers and tunable lasers. He is also interested in using these techniques for atmospheric sensing and monitoring and in statistical-mechanical calculation of partition functions and thermodynamic properties. In the 1980s he led the successful effort to analyze the complex spectroscopy of SF_6 , UF_6 , and CF_4 , and to apply these results to laser photochemistry, laser isotope separation, and molecular laser development.

McDowell has written 95 papers and several review articles, as well as the entry on "Infrared Spectroscopy" for the *McGraw-Hill Encyclopedia of Science & Technology*. He served as President of the Coblenz Society from 1987 to 1989 and has been active on editorial and conference organizing committees.

Dr. Thomas M. Orlando is a Senior Research Scientist in the Chemical Structure and Dynamics program. His main research interests are in gas-phase cluster ion (nanocrystal) reaction dynamics and in electron, photon, and hyperthermal ion-beam-induced surface chemistry. This work involves the use of a wide variety of low-energy ion-beam techniques such as radiofrequency guided beams (quadrupoles and octopoles), selected ion flow tubes, a 7-tesla ion cyclotron resonance mass spectrometer, and sensitive laser techniques such as laser-induced fluorescence and resonance-enhanced, multiphoton-ionization spectroscopy.

Before joining the MSRC, Orlando did postdoctoral work in the Solid State Sciences Division at Sandia National Laboratories. The first quantum-resolved studies of electron stimulated surface chemical reactions were carried out in collaboration with Dr. Alan Burns who has pioneered quantum-resolved, electron-stimulated desorption studies. Postdoctoral work in ion spectroscopy and photo-initiated intracluster ion-molecule reactions was also done with Professor J. P. Maier at the Institute for Physical Chemistry, University of Basel, Switzerland. Orlando's graduate studies, conducted under the direction of Professor S. L. Anderson at State University of New York, Stony Brook, concentrated on state-resolved studies of polyatomic ion-molecule reaction dynamics.

Orlando has written or contributed to 20 papers that discuss stimulated surface processes, ion-molecule reaction dynamics, and multiphoton spectroscopy. He has also given numerous invited presentations at national and international conferences and is a member of The American Physical Society and The American Vacuum Society.

Dr. Douglas Ray is a Senior Research Scientist in the Chemical Structure and Dynamics program. He is interested in developing a detailed understanding of intermolecular interactions and their effects on chemical dynamics. His current research focuses on the structure and dynamics of molecular clusters with experimental work involving combinations of techniques from mass spectrometry and optical spectroscopy. For example, he is currently using laser photoelectron spectroscopy, time-resolved fluorescence spectroscopy, and time-resolved multiphoton ionization spectroscopy in conjunction with cluster beams.

Prior to joining the MSRC in 1990, Dr. Ray was a post-doctoral research associate with Professor W. Carl Lineberger at the Joint Institute for Laboratory Astrophysics in Boulder, Colorado. There he used photofragmentation spectroscopy to study the structure and dynamics of ionic clusters. He received his Ph.D. in physical chemistry in 1985 from the University of California at Berkeley. His graduate research, under the direction of Richard J. Saykally, was in the area of high-resolution spectroscopy of van der Waals molecules and molecular ions using novel far-infrared laser absorption methods.

Dr. Ray has written or contributed to more than a dozen publications in cluster science. He has also given numerous invited presentations at national and international conferences and is a member of the American Chemical Society and the American Physical Society.

Greg A. Ritter joined the MSRC as a Technical Specialist in the Chemical Structures and Dynamics group in 1992. His interests include Fourier analysis, optical system design, and holography. He received his B.S. in laser optics engineering from the Oregon Institute of Technology, where his final project work involved optical pattern recognition.

Dr. Steven W. Sharpe is a Senior Research Scientist in the Chemical Structure and Dynamics program. He received his Ph.D. in physical chemistry from the State University of New York, Stony Brook, in 1986. Following postdoctoral work at the University of Southern California, he joined PNL in 1990. Sharpe's early research dealt with kinetic reaction studies of extraterrestrial atmospheres. His graduate studies, conducted under the guidance of Professor Philip Johnson, included the development of a novel technique for spectroscopic investigations of short-lived

and unstable gas phase chemical species. Postdoctoral studies, conducted under the auspices of Professor Curt Wittig, included the building and implementation of a laser laboratory for the study of weakly bonded, gas-phase molecules.

Sharpe is a member of the American Chemical Society. He has written or contributed to more than a dozen publications, the most recent of which appeared in advances in molecular vibrations and collisional dynamics.

Dr. X. (Sunney) Xie recently joined the MSRC's Chemical Structure and Dynamics program as a Senior Research Scientist. His current research interests are studying chemical physics in the condensed phases and biological systems using ultrafast laser techniques and conducting molecular spectroscopy at the nanometer scale on interfaces using near-field optical microscopy.

Xie received his Ph.D. in Physical Chemistry at the University of California, San Diego, in 1990. His graduate work, under the direction of Professor John Simon, involved picosecond time-resolved spectroscopic studies, most notably the development of a technique for conducting circular dichroism spectroscopy on the picosecond time scale and the application of this technique to study the conformational motion of myoglobin as well as electronic structures of photosynthetic reaction centers. Prior to joining the MSRC, Xie did postdoctoral studies with Professor Graham Fleming at the University of Chicago, where he constructed a fluorescence detection system with femtosecond time resolution and used it to study the electron transfer and energy transfer processes in photosynthetic systems.

Xie has written more than 20 publications and has given numerous presentations at conferences. He is a member of American Chemical Society, the Optical Society of America, and the Biophysical Society.

Environmental Dynamics and Simulation

Dr. James E. Amonette is a Senior Research Scientist in PNL's Earth and Environmental Sciences Center and part of the team responsible for the MSRC Environmental Dynamics and Simulation program. Since joining PNL in 1986, he has specialized in the areas of aqueous geochemistry and soil mineralogy.

Amonette's primary interest is in using proton-induced, x-ray emission; x-ray diffraction; infrared; and other spectroscopic techniques to characterize solid phases and to predict and monitor reactions associated with the disposal of hazardous wastes in soil environments. He received his Ph.D. in soil chemistry from Iowa State University in 1988.

Amonette is a member of the Clay Minerals Society, the International Soil Science Society, and the Soil Science Society of America. He has written or contributed to more than two dozen articles and other publications on topics such as oxidative weathering of micas, infrared spectroscopy of iron-chromium hydroxides, and synchrotron-based x-ray scattering studies of soil materials.

Dr. Ben P. Hay is a Senior Research Scientist in PNL's Earth and Environmental Sciences Center and a member of the MSRC Environmental Dynamics and Simulation Group. His current research interests center on the development and application of molecular modeling techniques for the elucidation of structure/activity relationships in coordination chemistry.

Prior to joining PNL, Hay held an appointment as a Postdoctoral Fellow with the Inorganic Structural Group at Los Alamos National Laboratory from 1989 to 1991. There he developed a molecular mechanics model for aqua, nitrate, and β -diketonato complexes of the f-block metal ions. This research was preceded by a two-year appointment as a Postdoctoral Fellow with Professor Athel L. J. Beckwith in the Research School of Chemistry, Australian National University.

Hay elucidated the detailed kinetics and mechanisms for intramolecular rearrangements of alkyl and alkoxy radicals in the liquid phase. This work led to the discovery of two new classes of alkoxy radical precursors.

Under the guidance of Professor Richard G. Finke, Hay received his Ph.D. in Chemistry from the University of Oregon, where his graduate research dealt with kinetic and mechanistic studies of the liquid-phase reactions of organo-cobalt compounds. He is member of the American Chemical Society and has written or contributed to more than a dozen publications on topics such as the thermolysis of coenzyme B₁₂, the reversible cyclization of the 5-pentylloxyl radical, synthesis of N-alkoxy-pyridine-2-thiones, and the molecular modeling of lanthanide complexes.

Dr. Charles J. Hostetler is a Senior Research Scientist in PNL's Earth and Environmental

Sciences Center and is a member of that center's liaison team to the MSRC. Since joining PNL, he has been involved in applications of geochemistry to contaminant transport. Hostetler's primary contributions have been in the development and application of reactive chemical transport models that include the effects of advection, dispersion, diffusion, aqueous speciation, adsorption, ion exchange, and solubility reactions on the mobility of solutes. His current research interests include the development of property estimation schemes for organic chemicals and uncertainty analysis for geochemical calculations.

Hostetler received his Ph.D. in planetary sciences at the University of Arizona in 1982. He has written or contributed to more than two dozen publications and reports on topics such as chemical transport models, geohydrochemical codes, and performance assessment analyses of waste disposal facilities.

Macromolecular Structure and Dynamics

Dr. Thomas S. Tenforde is Chief Scientist in PNL's Life Sciences Center and led the MSRC Macromolecular Structure and Dynamics program from 1988 to 1992. Prior to joining PNL in 1988, he spent 16 years at the Lawrence Berkeley Laboratory, most recently as leader of the Environmental Physiology program. Since 1980, Tenforde has served on two dozen national committees and boards and has been a reviewer for federal agencies, private organizations, and more than 20 refereed journals. He is a member of the American Association for the Advancement of Science, the New York Academy of Sciences, the Radiation Research Society, the Biophysical Society, and the Bioelectromagnetics Society (president in 1987-1988). He is currently a member of the National Academy of Sciences Board on Radiation Effects Research, the National Council on Radiation Protection and Measurements (Board of Directors), the American Conference of Governmental Industrial Hygienists, the IEEE Standards Coordinating Committee 28 on Nonionizing Radiation, and the International Nonionizing Radiation Protection Commission of the International Radiation Protection Association.

He chairs the National Research Council committee on the potential health effects of electromagnetic radiation from the Air Force's Ground Wave Emergency Network, and Committee 89 on Nonionizing Electromagnetic Fields of the National Council on Radiation Protection and Measurements.

Tenforde has written or contributed to 195 publications and reports and has presented 80 invited lectures at conferences and symposia during the last 10 years. He was recently an invited lecturer in the Electrical Engineering Department at Tokushima University in Japan, and at the International Radiation Protection Association's Second International Conference on Nonionizing Radiation held in Vancouver, British Columbia.

Tenforde attended Harvard University from 1958 to 1962, graduating with an A.B. degree *cum laude*. In 1959 he received the Harvard Dean's Honorary Scholarship. He was a National Institutes of Health (NIH) Predoctoral Fellow at the University of California-Berkeley from 1963 to 1968 and received his Ph.D. in biophysics in 1969. Tenforde was a Bay Area Heart Research Committee Postdoctoral Fellow at the University of California-Berkeley from 1969 to 1971 and an NIH Postdoctoral Fellow from 1971 to 1973.

Dr. Herman M. Cho is a Senior Research Scientist in the MSRC's Macromolecular Structure and Dynamics program. His work in his field of specialization--magnetic resonance spectroscopy--combines both theoretical projects and experimental, applied components, and encompasses both Nuclear Magnetic Resonance spectroscopy and time-domain Electron Paramagnetic Resonance spectroscopy. His current scientific activities center on the application of magnetic resonance methods to the elucidation of structure and dynamics in condensed matter, especially solids.

Prior to joining the MSRC in 1992, Cho was the holder of a Myron A. Bantrell Research Fellowship in Chemistry at the California Institute of Technology and a Postdoctoral Fellow of the U.S. National Science Foundation at the Eidgenössische Technische Hochschule in Zürich, Switzerland. Cho received his Ph.D. in chemistry from the University of California, Berkeley, as a student of Professor Alexander Pines. His A.B., also in chemistry, was awarded *magna cum laude* by Amherst College.

Dr. Gary P. Drobny, Professor of Chemistry at the University of Washington, has headed the MSRC NMR Program since 1991. He has primary responsibility for specifying the functional requirements of the several solids and liquids NMR systems being purchased or built as part of the EMSL project. He

also has the lead role in designing the radiofrequency pulsing system and console for the gigahertz NMR spectrometer.

Drobny has been affiliated with the University of Washington since 1981, when he became a faculty research associate and operations manager of the University's NMR laboratory. He became an Assistant Professor of Chemistry in 1985 and was promoted to the rank of full Professor in 1991. Drobny served as a member of the National Science Foundation's Advisory committee for Biological Facilities Centers from 1987 to 1990.

Drobny graduated *summa cum laude* with a B.S. in chemistry from San Francisco State University in 1976. He earned his Ph.D. in chemistry from the University of California-Berkeley in 1982. During the past five years, he has published 45 articles and reports in the field of NMR spectroscopy.

Dr. Charles G. Edmonds is a Senior Research Scientist in PNL's Chemical Methods and Separations Group and a member of the MSRC's Macromolecular Structure and Dynamics program. Edmonds joined PNL in 1988 and is jointly appointed in the Laboratory's Materials and Chemical Sciences and Life Sciences Centers. His university and institution-based research has involved instrument and methods development for biochemical and biomedical applications of mass spectrometry.

As a research student with Professor C.J.W. Brooks (Glasgow, Scotland) and subsequently in research appointments at the University of California-Berkeley (with Professor Melvin Calvin, Nobel Laureate) and at the Instituto Nacional de Pesquisas da Amazonia, Manaus, Brazil, Dr. Edmonds has investigated lipid biosynthesis in plant, marine, and mammalian (including newborn human) systems using high-resolution gas chromatography/mass spectrometry.

From 1980 to 1988, Dr. Edmonds was involved in a program of development and application of combined liquid chromatography/mass spectrometry based on the "thermospray" method of Dr. Marvin Vestal. In collaboration with Dr. Vestal, he developed, tested, and applied prototype interface devices to a variety of analytical problems in nucleic acid chemistry in the laboratory of Professor J. A. McCloskey.

The present focus of the research of Dr. Edmonds is the development and application of electrospray

ionization mass spectrometry (in combination with separation techniques) and tandem mass spectrometry for the detailed evaluation of the structure of substantially intact biopolymers. These studies include the development and use of the ion trap technique for mass analysis. Instrument and methods development in these studies is closely coupled to the questions of biochemical function which are addressed by these new structural probes.

Dr. Edmonds has authored or co-authored four books or book chapters and more than 50 publications on topics ranging from combined electrophoresis-electrospray ionization mass spectrometry of peptides and proteins to isolation and characterization of new modified nucleotide residues occurring in the transfer RNA of archaebacteria. He received his Ph.D. in organic chemistry at The University, Glasgow, Scotland, and is a member of the American Society for Mass Spectrometry, the American Chemical Society, and the Protein Society.

Dr. Alan L. Rockwood is a Senior Research Scientist in the MSRC's Macromolecular Structure and Dynamics program. His research involves investigations of structure, reactivity, and analysis of molecular and ionic species using a combination of experimental and theoretical methods. He is currently leading the development of advanced cell designs for ion cyclotron resonance mass spectrometry. He also recently developed a technique for studying fundamental properties of gas-phase ions by thermally induced dissociation. His theoretical work includes *ab initio* potential surface calculations on proton transfer reactions and simple model calculations on the dissociation of highly charged ions.

Prior to joining PNL, Rockwood was an applications chemist at JEOL, USA. He also worked as a mass spectrometrists at the University of Delaware, a research scientist at the University of Houston, and a faculty intern at the University of Utah. In addition, he has carried on independent research, which has resulted in the publication of three papers in *Physical Review* related to electrochemical thermodynamics.

Rockwood earned his Ph.D. in physical chemistry at Utah State University in 1981 under the direction of E. A. McCullough, Jr. He tested and disproved a previously proposed hypothesis for mode-selective chemistry for certain gas-phase isotope exchange reactions. As is characteristic of Rockwood's approach, his thesis research included both experimental (photo

chemical) and theoretical (*ab initio* potential surface and kinetic modeling) components aimed at solving a specific scientific problem.

Dr. Michael G. Sherman is a Senior Research Scientist in PNL's Chemical Methods and Separations group and a member of the MSRC Macromolecular Structure and Dynamics program. His research involves the design and development of the Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) and its applications for ultra-high resolution detection of large mass ions (e.g., biomolecules, clusters). He led the planning and development effort for the FT-ICR MS for MSRC. His activities also include the development of the electrospray ionization technique applied to the FT-ICR MS. His theoretical work includes trajectory calculations of ions in electric and magnetic fields.

Sherman received his Ph.D. in physical chemistry from the University of California at Irvine. His graduate work involved both the theoretical analysis of the FT-ICR MS technique and development of a laser desorption surface analysis technique coupled with FT-ICR MS detection. He spent two years conducting post-doctoral research at the Surface Science Center at the University of Pittsburgh. He is a member of the American Chemical Society, the American Physical Society, the American Society for Mass Spectrometry, the American Vacuum Society, and the American Association for the Advancement of Science. Sherman has been awarded one patent and has written or contributed to more than 25 refereed publications and books.

Dr. Richard D. Smith, Senior Staff Scientist, has been task leader for the separations and mass spectrometry component of the Macromolecular Structure and Dynamics program since 1988. He also serves as leader of the Chemical Methods and Separations Group in PNL's Chemical Sciences Department. For the past 5 years, his research has centered on the fundamental aspects and applications of advanced high-resolution methods and mass spectrometry and the development of new instrumental methods for structural characterization and analysis, particularly related to their use in basic environmental and biochemical research.

Smith has also been the principal investigator for programs studying high temperature kinetics, organized molecular assemblies in fluids, and fundamental

fluid phase and heterogeneous phenomena. In 1978, he was awarded the Bituminous Coal Research/R. A. Glenn Award for his work related to the mechanism of fly ash formation during combustion and trace element enrichment on fly ash surfaces.

Smith received R&D 100 Awards for the development of supercritical fluid chromatography-mass spectrometry (1983), the development of the first direct interface combining capillary zone electrophoresis with mass spectrometry (1988), and a process for materials formation from supercritical fluids (1988). He is the inventor or co-inventor on nine patents related to electrospray ionization, combined capillary electrophoresis-mass spectrometry and new processes for forming fine powders and thin films from supercritical solutions.

He has presented more than 125 plenary or invited lectures at national and international meetings. He was awarded an Associated Western University-DOE Distinguished Lectureship for the 1990-1991 academic year.

Smith received his Ph.D. in physical chemistry from the University of Utah. He is an Adjunct Professor at Washington State University and an affiliate faculty member of the Department of Chemistry, University of Idaho. He is a member of the American Chemical Society, the American Society for Mass Spectrometry, and the American Association for the Advancement of Science. Smith has been awarded seven patents and has written or contributed to more than 275 papers on mass spectrometry, separation processes, and supercritical fluids and their application to materials processing and separation methods.

Dr. Harold R. Udseth is a Senior Research Scientist in the MSRC's Macromolecular Structure and Dynamics Group. Since joining PNL in 1981, he has played an active role in the development of supercritical fluid technology, capillary electrophoresis (CE), electrospray ionization (ESI), and their combinations with mass spectrometry. He has used these techniques in the analysis of pesticides and herbicides; the analysis of complex mixtures and the separation of proteins; the sequencing of proteins and oligonucleotides; and fundamental studies of gas phase association reactions involving these materials. At present, he is participating in the development of several novel mass spectrometers while continuing his research in CE and ESI.

Udseth received his Ph.D. in physics in 1976 from the University of Minnesota. Prior to joining PNL, he was a research associate in the Chemistry Department at Brookhaven National Laboratory and the Chemistry Department of the University of Utah.

Udseth is the author or co-author of more than 50 publications. He has received two patents and an R&D 100 Award from *R&D Magazine*. He is a member of the American Chemical Society, the American Society for Mass Spectrometry, the American Physical Society, and the American Association for the Advancement of Science.

Materials and Interfaces

Dr. Jiri (Art) Janata joined the MSRC as Associate Director for the Materials and Interfaces program in 1991. Between 1987 and 1991, he was a professor in the University of Utah's Department of Materials Science and Engineering as well as the Director of the HEDCO Microengineering Facility. While at the University, Janata conducted research programs involving the development of novel chemical sensors, the development of microelectronic probes for medical applications, solid-state chemical sensors for air pollution control, and charge transfer at the liquid/liquid interface. During this period, Janata also was Visiting Professor at the Universität der Bundeswehr Munchen and EPFL Lausanne.

Janata received his Ph.D. (*summa cum laude*) in analytical chemistry from Charles University in Prague, Czechoslovakia, in 1965. He was a Visiting Fellow at Wolfson College, Oxford University from 1986 to 1987 and received the Humboldt Senior Scientist Prize in 1987 and the Heyrovsky Medal in 1990. He currently is a member of the editorial boards for *Sensors and Actuators*, *Biosensors*, *Sensor Technology*, and *Talanta*.

Janata is the author or co-author of more than a dozen book chapters and over 120 refereed publications. His book, *Principles of Chemical Sensors*, was published by Plenum Publishers in 1989 with a second printing in 1990. He also serves as a referee for organizations such as the National Institutes of Health, the National Science Foundation, and the Australian Research Council, and for publications such as *Analytica Chimica Acta*, the *Journal of American Chemical Society*, the *Journal of Inorganic Chemistry*, and *Biosensors and Bioelectronics*.

Janata has received more than a dozen patents. He is a member of the Electrochemical Society, the American Chemical Society, the Society for Electroanalytical Chemistry, and the American Association for the Advancement of Science. In 1992 he was one of the finalists in the International Science Pour L'Art competition sponsored by Hennessy and Louis Veritton.

Dr. Donald R. Baer is a Staff Scientist in PNL's Materials Research Section. Since joining PNL in 1976, he has specialized in the use of surface-sensitive techniques to examine effects of surface and interface chemistry on materials properties. He currently is principal investigator and group leader of a team developing the experimental components of the Materials and Interfaces program for the MSRC.

During 1984 and 1985, Baer was a Visiting Research Fellow in the Department of Materials Science and Engineering at the University of Surrey, Guildford, England. He is a member of the American Vacuum Society, is secretary of the Applied Surface Science Division, an associate editor of the *Journal of Vacuum Science and Technology*, and an associate editor of *Surface Science Spectra*. He is also a member of the American Physical Society, the Metallurgical Society of the American Institute of Metallurgical Engineers, the American Association for the Advancement of Science, and the American Society for Testing and Materials E42 Committee on Surface Analysis. He was Subcommittee Chairman for E42.02 (terminology) from 1984 to 1989 and is now serving as membership Secretary.

Baer received his Ph.D. in experimental solid-state physics from Cornell University in 1974 and did postgraduate work in the Department of Physics and Materials Research Laboratory at the University of Illinois, Urbana, between 1974 and 1976. He has written or contributed to more than 90 publications.

Dr. Cindy Bruckner-Lea is a Research Scientist with the MSRC's Materials and Interfaces Group. Her areas of expertise include chemical sensor research and development, electrical analysis using admittance and noise measurements, and thin film techniques such as Langmuir-Blodgett deposition and bilayer lipid membrane formation. She also is interested in biological effects of electromagnetic fields and scanning tunneling microscopy.

Bruckner-Lea joined PNL in 1992 after spending a year as a Postdoctoral Fellow at the University of Utah in the Materials Science and Engineering Department. During this period, she used scanning tunneling microscopy and electrochemistry to study compact organic films on sessile drops. She received her Ph.D. in Bioengineering from the University of Utah in 1990 and her B.S. in chemical engineering from the University of California, Davis, in 1985.

While at the University of Utah, Bruckner-Lea received the College of Engineering Scholarship in 1990, was elected to Phi Kappa Phi Honor Society in 1989, and received the Curtis C. Johnson Memorial Award for Outstanding Second Year Bioengineering Student in 1987. She also was awarded the four-year Carle C. Conway Fellowship while at the University of California, Davis. Bruckner-Lea has contributed to several journal publications in her field.

Dr. Scott A. Chambers is a Staff Scientist and Group Leader for the MSRC's Epitaxial Materials Synthesis Group. He is responsible for oversight of a research program in the epitaxial growth and characterization of materials relevant to several areas of environmental science. These areas include model geologic surfaces, novel catalysts for decomposition of halogenated hydrocarbons, inorganic ion exchanger surfaces, and advanced chemical sensors. He is also interested in the use of a variety of electron spectroscopic and diffraction techniques for both real-time and post-growth characterization of evolving epitaxial films, with an emphasis on direct, real-time feedback to materials sources in the growth chambers.

From 1987 to 1992, Chambers was a Senior Scientist at the Boeing High Technology Center, where he led a research effort in the epitaxy of intermetallic compounds on III-V semiconductors. Prior to that, he was Assistant and Associate Professor of Chemistry at Bethel College in St. Paul, Minnesota, and Research Professor in the Department of Chemical Engineering and Materials Science at the University of Minnesota.

Chambers received his A.B. and Ph.D. degrees in chemistry and physical chemistry from the University of California, San Diego, and Oregon State University, respectively. He has authored more than 60 refereed publications, book chapters, and review articles. He is a member of the Program Committee for the

Physics and Chemistry of Semiconductor Interfaces Conference and the Magnetic Interfaces - Physics and Characterization Symposium of the Materials Research Society. He is also Affiliate Professor of Materials Science and Engineering at the University of Washington.

Glen C. Dunham is the Senior Technical Specialist in the MSRC's Material and Interfaces Group. His education includes a master's degree in Materials Science from Washington State University and bachelor's degrees in physics and chemistry from Pacific Lutheran University where he was a President's Scholar and listed in *Who's Who in American Colleges and Universities*. He joined the MSRC in 1992 after ten years with WSU as a research scientist.

At WSU Dunham's specialty was metallorganic chemical vapor deposition of epitaxial films on semiconductor materials and processing the resulting structures into solar cells or laser-coupled photoconverters. His best converters exhibit the highest efficiencies ever reported. As a consultant he developed semiconductor lasers and transducers for high-frequency ultrasonic arrays. At PNL Dunham expects to continue metallorganic chemical vapor deposition but of oxides, sulfides, carbonates, and other mineral compounds in an effort to produce large crystalline surfaces for analysis and surface modification.

Mark H. Engelhard is a Senior Technical Specialist with the MSRC's Materials and Interfaces group. He joined PNL's Materials and Chemical Sciences Center in 1980 and has more than 13 years research experience in the use of surface analysis techniques for the examination of materials surface chemistry. He is experienced in using Auger electron spectroscopy, x-ray photoelectron spectroscopy, secondary ion mass spectroscopy, Rutherford backscattering spectroscopy, nuclear reaction spectroscopy, and particle-induced x-ray emission techniques.

Engelhard also has designed and modified specialized experimental apparatus for surface science studies, and he maintains the calibration and repair of surface analysis systems used by the MSRC staff. He has contributed to a number of publications in his area of expertise. Engelhard received his A.A. degree in Applied Science from Columbia Basin College in 1978.

Dr. Jay W. Grate joined the MSRC's Materials and Interfaces program as a Staff Scientist in 1992. From 1984 to 1992, he worked as a Research Chemist at the Naval Research Laboratory in Washington, D.C., including a year's sabbatical at The Scripps Research Institute in La Jolla, California. His interests include topics in organic chemistry, inorganic chemistry, organometallic chemistry, surface science, and biomimetic systems, with current research emphasizing organic thin films, polymers, molecular recognition, surface science and sorption equilibria as they apply to the development of chemical sensors. He has also done research in organolanthanide chemistry, carbon-skeleton rearrangements of organocobalt vitamin B₁₂ derivatives, and catalytic antibodies.

Grate earned his Ph.D. in chemistry at the University of California, San Diego in 1983, his M.S. in chemistry at the University of California, San Diego in 1980, and his B.A. (*summa cum laude*) from Rollins College in 1978. He was a National Science Foundation Pre-doctoral Fellow at the University of California, San Diego; a National Merit Scholar at Rollins College; and was awarded Outstanding Senior Scholar at Rollins College. He has written or contributed to more than 100 scientific and technical papers and presentations. He is a member of the American Chemical Society and the Electrochemical Society, and serves as a member of the Executive Committee of the Sensors Group in the Electrochemical Society.

Dr. Michael A. Henderson is a Senior Research Scientist in the Materials and Interfaces program. He specializes in the surface chemistry of metal and metal oxide materials under ultrahigh vacuum conditions and examines the structure, dynamics, and reactivity of simple chemical systems at single-crystal surfaces with molecular-level probes such as electron energy loss, secondary ion mass, and Auger electron spectroscopies. The goal of this research is to understand the complex chemistry of environmentally related surface phenomena.

Before joining the MSRC in 1991, Henderson was a postdoctoral researcher at the University of Pittsburgh, where he examined electron- and photon-stimulated processes at metal surfaces. This research yielded interesting results about the anisotropic nature of low-frequency adsorbate vibrations at atomic-high steps. Such vibrations are believed to be the precursors to processes such as surface diffusion and reaction.

Henderson obtained his Ph.D. in physical chemistry in 1988 from the University of Texas, Austin, under the direction of J. Michael White. He has written or contributed to 40 publications on topics including organophosphorus surface chemistry, Fischer-Tropsch catalysis, and surface photochemistry. He is a member of the American Vacuum Society, the American Chemical Society, and the Materials Research Society.

Dr. Mirosława (Mira) Josowicz, a Research Scientist in PNL's Materials and chemical Sciences Center, is assigned to the Materials and Interfaces program. Her area of interest includes the use of electrochemical techniques to the synthesis of novel materials. The materials can be involved in biomimetic programming and in the development of chemical sensors. Josowicz is principal investigator of a project on novel electrosynthesis of organic electroactive polymers with organo-substituted cyclic trimeric phosphazenes as a dopant. Possible applications of these materials could include protective coatings for solar cells or insulating dielectric layers for integrated circuits.

Prior to joining PNL, Josowicz was a researcher at the University of Bundeswehr in Munich, Germany. While at the University, she conducted a research project involving the development of conducting organic polymer as chemically sensitive layers to detect organic vapors in potentiometric solid-state sensors. This study of the interactions between the sensitive layers and the organic vapors contributed to the basic understanding of the sensing principles.

Josowicz received her Ph.D. in chemistry from the Technical University in Munich under the direction of Professor K-E Quentin. She received the Alexander von Humboldt Research Scholarship in 1983 and subsequently was a Visiting Associate Professor in the Bioengineering Department at the University of Utah-Salt Lake City, where she was involved with a chemical sensor project.

Josowicz has received seven patents and written or contributed to 30 publications and eight book chapters on various aspects of organic polymers and their application; i.e., for encapsulation of semiconductor devices or as ion-exchange membranes in amperometric sensors. She is a member of the German Chemical Society, the Electrochemical Society, and the Society for Electroanalytical Chemistry.

Dr. John P. LaFemina is the Program Manager for the Materials and Interfaces program. He joined the MSRC as a Senior Research Scientist in the Materials Theory Group in 1989. His research seeks a comprehensive understanding of the physics and chemistry of insulator and semiconductor surfaces important in areas as diverse as the design of advanced electronic materials, the development of chemical sensor and separations technologies, and subsurface contaminant transport. Between 1985 and 1989, LaFemina was a Captain in the United States Army, serving as the Deputy Director of the Science Research Laboratory and the Thomas H. Johnson Photonics Research Center.

In addition to the modeling of surface structure and chemistry, LaFemina's other interests include heteroepitaxial gas phase and solution crystal growth, modeling the structure and photophysics of thin film polymers, and investigating the morphological dependence of the electronic structure for molecular and periodic systems.

LaFemina earned his Ph.D. at The Pennsylvania State University under the direction of Dr. John P. Lowe in 1985. He has written or contributed to more than 90 papers and presentations on topics ranging from the photophysics of polyimide and poly(ethylene terephthalate) to the atomic and electronic structure of semiconductor and mineral surfaces and interfaces. He is the Series Editor of "The Chemistry and Physics of Surfaces and Interfaces" published by CRC Press, and a member of the American Chemical Society, the American Physical Society, the American Vacuum Society, the Materials Research Society, and the Mineralogical Society of America.

Dr. Delbert L. Lessor, a Staff Scientist in the Applied Physics Center, spends 25 percent of his time on MSRC materials synthesis activities. His special interests include fundamental surface science and environmental remediation, and he has experience in basic and applied work in both areas. Lessor has participated in deducing structure of molecular adlayers on a number of materials using low energy electron diffraction, with emphasis in these studies shifting from electronic materials to those that are environmentally relevant.

He also models contaminant motion and holdup in soil and groundwater, where the fundamental interactions at soil particle surfaces are key to remediation schemes such as steam stripping, *in situ* Joule heating, and *in situ* vitrification.

Lessor joined PNL in 1967 after receiving his Ph.D. from Kansas State University. He has developed models and performed computations in diverse areas such as (alpha, neutron) nuclear reactions, electrical phenomena in filtration, phasecontrast microscopy, and multi-electrode multiphase Joule heating.

Dr. Charles H.F. Peden recently joined the MSRC as Staff Scientist and Technical Group Leader for Surface Chemistry in the Materials and Interfaces Program. His main research interests are in the kinetics and mechanisms of surface chemical reactions important in heterogeneous catalysis, materials synthesis, separations, and adhesion. Many of his studies involve the use of a coupled high-pressure reactor/ultra-high vacuum (UHV) surface science apparatus to measure reaction rates on well-characterized, single crystal model catalysts. He uses both in- and ex-situ (UHV) spectroscopies in conjunction with the kinetic measurements to develop mechanistic models.

After graduating with distinction from California State University, Chico, with a B.S. in chemistry, Peden completed his Ph.D. in physical chemistry at the University of California, Santa Barbara, under the direction of Ralph G. Pearson. He then spent two years as a postdoctoral associate at Sandia National Laboratories in Albuquerque, New Mexico, before joining the scientific staff. He spent the next 7 years at Sandia as a senior member of the technical staff in the Inorganic Materials Chemistry Department.

Peden has written or contributed to more than 70 publications on topics such as automobile exhaust catalysis, hydrocarbon reforming on bimetallic catalysts, the structure of hydroprocessing catalysts, the kinetics of silicon nitride thin-film growth, and adhesion at metal/oxide interfaces. He is a member of the American Vacuum Society, American Chemical Society, Materials Research Society, and the North American Catalysis Society. He is also the Technical Director for Short Courses of the American Vacuum Society.

Dr. Barry M. Wise joined the MSRC's Materials and Interfaces program as a Senior Research Scientist in 1992. He first joined PNL in 1982, working in

the Waste Technology Center in liquid-fed ceramic melter and waste decontamination process development. His research interests include elucidating behavior of biased regression methods, particularly with respect to modeling dynamic systems.

Wise graduated from the University of Washington in 1982 with B.S. degrees in chemistry and chemical engineering. He received his M.S. degree in chemical engineering from the University of Washington in 1987 and his Ph.D. in chemical engineering in 1991. He is an adjunct lecturer in Chemical Engineering at Washington State University at Tri-Cities. Dr. Wise has five articles in peer-reviewed journals, more than 20 presentations and conference proceedings, and a software package in the public domain.

Theory, Modeling, and Simulation

Dr. Thom H. Dunning, Jr., became Associate Director for the MSRC Theory, Modeling, and Simulation program in 1989. Before joining the MSRC, he was Senior Scientist and Group Leader of the Theoretical and Computational Chemistry Group and Head of the Chemical Dynamics Program at Argonne National Laboratory. Dunning is an Adjunct Professor at Washington State University and an Affiliate Professor at the University of Washington.

Dunning has written or contributed to nearly 100 publications on topics ranging from advanced techniques for molecular calculations (including the development of molecular basis sets and generalized valence bond theory) to applications involving the photophysics of atmospheric species and exotic laser molecules, and chemical reactions involved in combustion. More recently, he has been involved in modeling the structure and energies of ion-water clusters and the effects of solvation on the energetics and dynamics of chemical reactions.

Dunning is a member of the American Chemical Society and is a Fellow of the American Physical Society and the American Association for the Advancement of Science. Since 1987, he has been the Series Editor for *Advances in Molecular Electronic Structure Theory* published by JAI Press, Inc. Currently, he is a member of the Executive Committee of the Energy Research Supercomputer Users' Group, the National Science Foundation's Chemistry Advisory Committee, and the Policy Board of the Concurrent Supercomputer Consortium.

Dunning was awarded a Woodrow Wilson Fellowship in 1965-66 and a National Science Foundation Fellowship in 1966-69. He received his B.S. in chemistry from the University of Missouri-Rolla in 1965 and his Ph.D. in chemical physics from the California Institute of Technology in 1969.

Dr. Raymond A. Bair is Senior Technical Program Manager for Theory, Modeling, and Simulation. He leads the MSRC's Molecular Science Software group. The group's present work is focused on development of electronic structure and molecular dynamics codes for massively parallel computers; graphical user interfaces for computational chemistry codes; graphical visualization and analysis tools; and molecule knowledge systems. The group is also a principal contributor to the design and specification of the Molecular Science Computing Facility.

From 1987 to 1990, Bair was director of new product development with BioDesign Inc., which produced interactive molecular modeling and simulation tools for the chemical industry. Prior to 1987, Bair was an Assistant Scientist and postdoctoral fellow at Argonne National Laboratory, where he studied the energetics and mechanisms of combustion reactions and developed *ab initio* computational methods for vector and parallel computers.

Bair received his Ph.D. in theoretical chemistry from the California Institute of Technology in 1981. He is a member of the DOE Energy Sciences Network Steering Committee, the American Chemical Society, American Association for the Advancement of Science, and Sigma Xi. In 1979, he received the Lazlo Zechmeister Fellowship, and from 1976 to 1979 he completed a National Institutes of Health traineeship. He has written or contributed to more than a dozen publications in his field.

Dr. L. René Corrales is a Senior Research Scientist in the Theory, Modeling, and Simulation group. His research program examines the thermodynamic and mechanical properties of complex condensed matter systems via statistical mechanical methods. His research emphasizes the development of theoretical models and simulation methods to study interfacial phenomena and dissolution processes of amorphous materials immersed in water. He is studying the interplay and relationship between microscopic structure and macroscopic phenomena using a collection of available methods to develop, solve, and implement

both analytic and simulation techniques. These complementary methods are used to overcome the limitations and specific difficulties that complex systems present when formulating and solving theoretical models. This work includes the study of phase transitions and critical phenomena in polymer solutions; the simulation of polymerizing and network-forming systems such as selenium and silica systems; and the development of methodologies to examine epitaxial growth and diffusion processes on surfaces.

Corrales is a member of the American Physical Society and the American Chemical Society. He was awarded a National Science Foundation Fellowship in Chemistry in 1989-91. He earned his B.S. in chemistry from the Massachusetts Institute of Technology in 1982 and his Ph.D. in chemical physics from the University of California, San Diego, in 1988.

Dr. Liem X. Dang joined the MSRC Theory, Modeling and Simulation program as a Senior Research Scientist in 1991. Previously, he was a Visiting Scientist at the IBM Research Division in San Jose, California and a Postdoctoral fellow at the University of California, San Francisco.

Dang received his Ph.D. in theoretical chemistry in 1985 from the University of California, Irvine, where his advisor was Professor Max Wolfsberg. Dang's research interest focuses on molecular dynamics simulation of chemical and physical processes. He has written or contributed to more than 20 articles on topics such as protein stability, ionic clusters, and ionic solutions, including the development of nonadditive intermolecular potentials for water-water and ion-water interactions. Dang is a member of the American Chemical Society.

Dr. David F. Feller joined the MSRC as a Senior Research Scientist in 1989. Between 1984 and 1989, he was a Research Associate Scientist and Manager of the Chemistry Computational Facility at Indiana University. His primary areas of research interest are the development and application of techniques for the theoretical investigation of ground-state and excited-state potential energy surfaces as well as the study of molecular properties.

During his academic career, Feller was awarded a Collins Radio Scholarship and the Regents Competitive Scholarship while at Loras College in Dubuque, Iowa. Subsequently, he received a Proctor and

Gamble Scholarship. He earned his Ph.D. in physical chemistry at Iowa State University in 1979 under Professor Klaus Ruedenberg.

Feller has written or contributed to more than 60 articles. Most recently, these have included studies of the hyperfine parameters in small radicals and the calculation of momentum distributions for comparison with electron momentum spectroscopy. He is currently involved in a project to build graphical user interfaces for computational chemistry applications.

Dr. Bruce C. Garrett is a Staff Scientist and Technical Group Leader of Molecular Theory and Modeling Group. Before joining the MSRC in 1989, he was a founder and research scientist at Chemical Dynamics Corporation, where his responsibilities included developing and directing basic research in theoretical physical chemistry.

Garrett has been actively engaged in research involving theoretical and computational chemistry, particularly in the field of the dynamics of atomic and molecular collisions. He has been a key participant in the development of variational transition state theory (VTST), a practical and reliable method for predicting rate constants for gas-phase chemical reactions. He has written or contributed to more than 100 publications on a variety of topics including gas-phase reaction dynamics, translational-to-rotational and translational-to-vibrational energy transfer in gas-phase collisions, quenching of electronically excited states in gas-phase and gas/surface collisions, and chemisorption and diffusion of hydrogen on metal surfaces. Since joining the MSRC, he has initiated a research program to study solvent effects on chemical reactions using VTST methods.

Garrett received his Ph.D. in physical chemistry from the University of California, Berkeley, in 1977. He is a member of the American Chemical Society and the American Physical Society. He has served as a committee member on the National Research Council Review Panel for the AFOSR High Energy Density Materials program since 1990.

Dr. Anthony C. Hess became a full-time MSRC Senior Research Scientist in 1991, after spending two years with the organization as a Postdoctoral Fellow. Hess earned his Ph.D. in Chemistry at Arizona State University in 1988. His graduate research was a combination of theoretical and experimental studies

in the fields of solid state chemistry and geochemistry. During this time, he was vice president of Phi Lambda Upsilon, the Honor Chemical Society. He received his B.S. in Chemistry from North Dakota State University in 1984.

Since joining the MSRC, Hess has initiated a research program that both uses and develops state-of-the-art *ab initio* solid-state quantum chemistry methods for studying complex mineral systems. Hess' ongoing collaboration with the authors of CRYSTAL involves the development and testing of new approaches in periodic Hartree-Fock theory. Hess' research group is focused on implementing new theoretical methods for studying the physical properties of a range of environmentally and catalytically important materials. These include a diverse class of materials from minerals (e.g., clays, zeolites, and other oxides) to different types of hydrated ices.

Hess is a member of the American Physical Society, the American Chemical Society, the American Geophysical Union, and the American Mineralogical Association. In 1991, Hess has presented invited lectures on "Periodic Hartree-Fock Theory of Low Symmetry Systems: Applications and Perspectives" (Orsay, France), "Ab Initio Methods in Geochemistry and Mineralogy" (Arizona State University), and "Experimental and Theoretical Investigations of the Mineral Kaolinite" (American Chemical Society).

Dr. Rick A. Kendall is a Senior Research Scientist in the Molecular Science Software Group interested in developing portable modern *ab initio* quantum chemistry codes on advanced architectures. In FY 1989, he was a Postdoctoral Appointee with the Theoretical Chemistry Group at Argonne National Laboratory's Chemistry Division. In FY 1990, Kendall joined the MSRC as a research scientist in the Theory, Modeling, and Simulation program.

In 1983 Kendall graduated *magna cum laude* from Indiana State University and as a member of Phi Kappa Phi. In 1987 at the University of Utah, he received the Stauffer Graduate Research Prize and the Graduate Research Fellowship. He earned his Ph.D. from the Chemistry Department at the University of Utah in 1988.

Kendall is a member of the American Chemical Society and the American Physical Society. He has performed and presented research that encompasses vibration-rotation-induced electron detachment of

molecular anions, clusters of molecular anions, analytic evaluation of non-Born-Oppenheimer matrix elements, electron affinities of first row atoms, and parallelization of *ab initio* software on both distributed workstations and on traditional parallel supercomputers.

Dr. Maureen I. McCarthy joined the MSRC in January 1991 as a Senior Research Scientist. From 1988 to 1991, McCarthy was awarded a fellowship from the Lady Davis Fellowship Trust to pursue postdoctoral research at the Hebrew University in Jerusalem, Israel. She earned her Ph.D. in Chemistry from the University of Colorado in 1988. Her thesis work combined experimental and theoretical techniques in photochemistry. During her graduate studies, she worked at the Fachbereich Chemie Universitat in Frankfurt, Germany, as a NATO Visiting Scientist and was awarded a Doctoral Fellowship by the University (1983-1984). She received her B.S. in Chemistry from Boston College in 1983 (*magna cum laude*, Phi Beta Kappa).

McCarthy's research interests are in modeling heterogeneous processes that occur at solid surfaces. Her work includes studies on environmentally important systems found in the subsurface and the atmosphere. She is currently involved in an effort that combines methods of *ab initio* solid-state quantum chemistry and classical mechanics to study interfacial dynamics. One goal of this work is to characterize the behavior of contaminants on mineral surfaces.

McCarthy is a member of the American Chemical Society, the American Physical Society, and the American Geophysical Union. She maintains collaborations and has published articles with colleagues in experimental and theoretical chemistry, physics, and geochemistry.

During 1991, McCarthy has given presentations or invited lectures at the West Coast Theoretical Conference, the Oregon Graduate Institute, the Northwest Regional Meeting of the American Chemical Society, and the Annual Fall Meeting of the American Geophysical Union.

Dr. John B. Nicholas is a Senior Research Scientist with the MSRC's Theory, Modeling, and Simulation program. Prior to joining Battelle in 1991, Nicholas spent seven years at Argonne National Laboratory.

While assigned to the Department of Biology, in collaboration with Drs. Charles Ehret and Kenneth Groh, Nicholas wrote computer programs for unique statistical analysis and graphics of time series data resulting from experimental studies in chronobiology. Next, he was assigned to the Theoretical Chemistry Group. Under the direction of Drs. Thom Dunning and Albert Wagner, Nicholas wrote user interfaces to *ab initio* computer programs; vectorized and parallelized computer codes; and created new ways of viewing potential energy surfaces and normal mode vibrations by programming Macintosh and DEC computer graphics.

Nicholas's final assignment at Argonne was with the Department of Chemistry. In collaboration with Dr. Lennox Iton he conducted research involving the structure and dynamics of zeolites and the interaction of zeolites with organic molecules. He wrote a user-friendly computer simulation package for molecular dynamics, energy minimization, normal-mode analysis, force field fitting, data analysis, and graphics of chemical systems that functions on a variety of supercomputers and workstations (20,000+ lines of code). He also performed *ab initio* studies of zeolite structure and acidity and developed molecular mechanics force fields using *ab initio* computations in conjunction with experimental data.

Nicholas received his Ph.D. in physical chemistry, specializing in computational chemistry, from the University of Illinois at Chicago in 1991 and his B.S. (*cum laude*) in biochemistry from Illinois Benedictine College in 1986. He is proficient in programming and using Cray, Alliant, Ardent, Silicon Graphics, IBM-RS/6000, DEC, Macintosh, Unix, VMS, X-Windows, FORTRAN, C, CHEMLAB, BIOGRAF, GAUSSIAN, GAMESS, HONODO, MOPAC, CONCORD, and GRAMPS and has contributed to several publications in his field.

Dr. Rick L. Ornstein joined the MSRC as a Senior Research Scientist in 1988 and was appointed Adjunct Associate Professor in Chemistry at Washington State University in 1990. He was promoted to Staff Scientist at PNL in 1991, and in 1992 he was appointed Visiting Professor of Biophysics at Roswell Park Cancer Institute in Buffalo, New York. From 1985 to 1988, he was a research scientist with Kodak in the Health and Nutrition Department where he set up a peptide/protein modeling and simulation research laboratory. From 1982 to 1985, he was

a research staff member/lecturer at Princeton University in the Biochemistry Department.

After receiving his Ph.D. in Biophysical Sciences from the State University of New York, Buffalo, in 1979, he took a postdoctoral fellowship from 1979 to 1982 in the research group of Professor Jacques R. Fresco in the Biochemistry Department at Princeton University. He received his masters degree in Environmental Health Sciences in 1974 from the City University of New York at Hunter College and his B.A. from the City University of New York at Queens College in Physics in 1972 with minors in biology and chemistry. Ornstein was awarded fellowships during his master's, doctoral, and postdoctoral studies.

Ornstein has published more than 50 papers in the areas of structure/function/dynamic relationships of peptides, proteins, nucleic acids, and rational enzyme redesign. He is a member of the American Chemical Society, the Hazardous Materials Control Research Institute, the Protein Society, the Society of Environmental Toxicology and Chemistry, the AAAS, and is listed in *Who's Who in Science and Engineering*.

Dr. Gregory K. Schenter joined the MSRC in 1988 after receiving his Ph.D. in applied physics from Cornell University under the direction of Dr. Richard L. Liboff. At Cornell, his research interests concentrated on classical and quantum transport of charge-carriers in plasmas and semiconductors. Prior to his Ph.D. work he gained experience in both pure and applied physics developing statistical analysis of fission product yield and nuclear decay heat data in addition to the modeling of dye laser physics, reactor physics, and material flows.

His current research interests include the theoretical modeling of chemical dynamics as it occurs in the condensed phase. This work has ranged from the study of fundamental aspects of simplified systems to more realistic systems which may be directly verified by experiment.

He has written over a dozen papers in the areas of nuclear, plasma, semiconductor, and chemical physics.

Dr. David M. Sherman recently joined the MSRC as a Staff Scientist in the Theory, Modeling, and Simulation Group. From 1984 to 1991, he was with the U.S. Geological Survey, where his research focused on the electronic structures and spectra (optical

absorption and Mossbauer) of minerals. Over the past two years, he has been using electronic structure calculations to predict pressure-induced phase transitions and elastic properties of oxides and silicates. His recent interests have extended to bonding on mineral surfaces and the behavior of water in minerals.

To date, Sherman has authored more than 25 journal articles and book chapters primarily on the electronic structures and optical spectra of transition metal oxides and silicates. A number of his papers are concerned with pressure-induced changes in chemical bonding and their effects on the physics and chemistry of the earth's deep interior.

Sherman received his B.A. in chemistry (with highest honors) and B.S. in earth sciences from the University of California, Santa Cruz in 1980. He was awarded his Ph.D. in geochemistry in 1984 by the Massachusetts Institute of Technology, where he also held a brief postdoctoral appointment.

Sherman is a member of the American Geophysical Union and the Mineralogical Society of America (MSA). He has served on several MSA committees and currently is an Associate Editor of *American Mineralogist*. In 1989, Sherman was appointed an Adjunct Professor at the University of Colorado, Boulder; and in 1991, he was awarded the F. W. Clarke Medal of the Geochemical Society for his work on the mineralogical applications of quantum chemistry.

Dr. Mark A. Thompson recently joined the MSRC as a Senior Research Scientist. Prior to joining the MSRC, he was an Assistant Chemist at Brookhaven National Laboratory. His primary research interests include the theoretical investigation of electron transfer in photosynthetic systems, electronic structure of cofactors and active sites in proteins, and model Hamiltonians useful for studying biological systems. This research includes developing electronic structure and molecular dynamics methods for parallel computing environments.

Thompson received his Ph.D. in physical chemistry in 1990 from the quantum Theory Project at the University of Florida. His research advisor was Dr. Michael Zerner. He graduated *summa cum laude* from the University of Minnesota with B.S. in biology in 1983. He did his undergraduate research with Dr. Peter Chapman and Dr. Stan Dagley on the catabolism of aromatic compounds by soil bacteria.

While at the University of Minnesota, Thompson was awarded the Alumni Society Scholarship and the Novy Miller Scholarship. In 1984, he received a National Science Foundation Predoctoral Fellowship; and in 1989, a Shell Oil Fellowship. He is a member of the American Chemical Society and Phi Beta Kappa. He has written or contributed to a dozen publications. In 1991, he was an invited speaker at the Sanibel Symposium on Quantum Chemistry and Quantum Biology.

Dr. Sotiris S. Xantheas became a full-time MSRC research scientist in 1992 after spending two years with the organization as a Postdoctoral Fellow. Xantheas earned his Ph.D. in physical chemistry from Iowa State University, where his research advisor was Professor Klaus Ruedenberg. His graduate research involved the computation of potential energy surfaces for various chemical reactions using correlated wavefunctions, the elucidation of reaction paths governing carbene ring opening processes as well as the location and characterization of intersections of potential energy surfaces of the same symmetry in polyatomic systems.

During his academic career, which included two appointments as instructor at Iowa State University, Xantheas was awarded the American Chemical Society's Alpha Chi Sigma Chapter award for excellence in graduate research, the Iowa State University teaching excellence award, and the Chemistry Department's outstanding teaching award. He earned a diploma in Chemical Engineering from the National Polytechnic University of Athens, Greece. During his senior year he was a fellow of the Austrian Federal Ministry for Science and Research at the Institute for Analytic and Inorganic Chemistry of the University of Innsbruck, Austria.

Xantheas' current research interests include modeling of atmospheric sulfur chemistry and the study of the structures, properties, and energetics of small ion-water clusters and their impact in the understanding of the general problem of the solvation of ions. He has written or contributed to more than a dozen articles on topics such as intersections of potential energy surfaces, reaction mechanisms and structures, and energetics of small ion-water clusters. He is a member of the American Chemical Society.

Computing and Information Sciences

Ms. Janice R. Lewis is Senior Technical Program Manager in the MSRC Computing and Information Sciences program and a Staff Scientist in PNL's Applied Physics Center. Lewis joined PNL in 1977 and has extensive experience in system analysis, system design, and application development. Software development projects for which she has been principal investigator include command and control systems for the U.S. Army as well as emergency response systems for the Hanford site.

Ms. Lewis has managed several software integration projects including the technical management of VISTA, a PNL initiative.

Prior to joining PNL, Lewis worked for Washington State University as a software developer and for Boeing Computer Services as a systems analyst.

Lewis earned her M.S. in Computer Science from Washington State University and her B.S. in mathematics from the University of Idaho.

Mr. Gordon A. Anderson is a Senior Research Engineer in PNL's Applied Physics Center and is assigned to the MSRC Computing and Information Science program. He is responsible for the design and development of automated control systems and data acquisition systems, which require extensive use of microprocessor technologies. Some of the systems developed by Anderson as part of Applied Physics Center programs have flown on the NASA space shuttle.

Anderson has analog and digital circuit design experience as well as extensive working knowledge of the Intel 80X86 and Zilog Z80 architectures. He also is experienced in the development of specialized robots and in the application of industrial robots to specific problems. Anderson has developed a presentation on robotics that has been given to more than 500 students and adults as part of PNL's Sharing Science with Schools Program.

Prior to joining PNL, Anderson worked for Exxon Nuclear on the Laser Isotope Separation Project and at the Fuels Fabrication Plant. During this period, he developed instrumentation and automation equipment.

Anderson received his B.S. in electrical engineering from Washington State University. His publications include a design concept that was featured in EDN Magazine and won a Readers' Choice Award.

Mr. Douglas W. Arlt became a member of the MSRC's Computing and Information Sciences program this year to help develop data acquisition systems for the Chemical Structures and Dynamics Group. He has written both DOS and Windows applications for the PC-based systems using "C" language and is interested in digital design.

Arlt first worked at PNL in 1987. During his senior year in high school he participated in the Laboratory's Inquiry Into Science Program. Between 1987 and 1992, he was a full-time PNL employee every summer, while he pursued his B.S. degree in electrical engineering at Walla Walla College. His computer programming skills were used on projects such as a robotic mannequin, printed circuit board repair, and reverse engineering.

Mr. Peter R. Berard is a Research Scientist in the EMSL Computing Group, concentrating on mass storage systems. Currently, Berard is participating in designing and developing a DataBase Computer System that will provide intelligent data archiving capabilities within the EMSL computing environment. He is sharing his knowledge by actively participating in the IEEE Storage Systems Standards Working Group. Berard is also participating as an observer to both the Executive Committee and Technical Committee of the National Storage Laboratory's High-Performance Storage System (HPSS) project at Lawrence Livermore National Laboratories.

Over the past 8 years, Berard has designed, developed, and managed large- and small-scale software systems on various UNIX O/S-based platforms. Berard received his B.S. in Computer Science (Scientific Option) from the University of Southwestern Louisiana in 1985. He has recently authored a paper describing his work for the 1993 Goddard Conference on Mass Storage Systems and Technologies.

Mr. D. Michael DeVaney is a Senior Research Scientist in PNL's Applied Physics Center. Currently, he is assigned to the MSRC Computing and Information Sciences program and is responsible for the Information Management Task for the EMSL

Project. This task involves the acquisition, implementation, and integration of a scientific data-base system and a high-performance hierarchical archival system. The system must be capable of managing up to a few tens-of-terabytes of data with extensive database access and file transfer rates in many tens-to-hundreds of megabytes per second. Object database research support for this task is being conducted at the Oregon Graduate Institute.

Since joining PNL in 1987, DeVaney has specialized in object-oriented and knowledge-based systems, including knowledge engineering and systems analysis, object database, object-oriented programming, rule-based expert systems, and blackboard systems. His research interests also include hypertext/hypermedia systems and parallel processing. As a member of the Applied Physics Center staff, DeVaney has been a major contributor to the development of a knowledge-based tactical decision aid; a model-based reasoning expert system; a methodology to integrate knowledge-based systems with conventional tactical battle management systems; and an electronic laboratory notebook.

DeVaney received his B.S. in mathematics from the University of Washington in 1972. He has since attended Syracuse University and the Massachusetts Institute of Technology. His most recent publications are included in *Proceedings of the DARPA Open Object-Oriented Database Workshop II*, which was held in Dallas, Texas in September 1991; *Proceedings of the Human Factors Society, 35th Annual Meeting*, which also was held in September 1991; and *Proceedings of the Sixth International Working Conference on Statistical and Scientific Database Management*.

Mr. George I. Fann, a research scientist, joined the MSRC's Computing and Information Sciences program in 1991. Since then, he has worked on eigen-system solvers for parallel supercomputers and participated in algorithm developments for parallel numerical methods and visualization for fluid dynamics. He also has a continuing interest in algebraic geometry and number theory.

Fann received an S.M. degree in mathematics from Massachusetts Institute of Technology and an A.B. degree in mathematics from the University of California-Berkeley. He is a member of Phi Beta Kappa and the American Mathematical Society.

Mr. Marc H. Johnson is a Research Engineer in PNL's Applied Physics Center and is assigned to the MSRC's Computing and Information Sciences program. He is responsible for the design of high-speed data acquisition systems, computer control systems, portable electronic devices, and high-voltage power supplies.

Johnson has extensive digital circuit design experience, including work with the AM29000 32-bit RISC processor and the design of high-speed digital filters. He has also designed lighting systems, linear power supplies, and photovoltaic power systems. In addition, he developed optical diagnostic methods for the plasma etching of semiconductors.

Before joining PNL, Johnson worked at the Manuel Lujan Space Telemetry center, where he designed part of a communication system for NASA's Tracking and Data Relay Satellite System. Johnson earned his M.S. and B.S. in electrical engineering at New Mexico State University.

Dr. Donald R. Jones has been a Staff Engineer in PNL's Applied Physics Center since 1989. Currently, he is assigned to the MSRC Computing and Information Sciences program and is the Visual Engineering Task Leader. His team provides general-purpose computer graphic resources and visual computer tools for all MSRC scientists. His research interests include scientific visualization, graphical user interfaces, data fusion, video technology for the sciences, multimedia for scientific presentations, and scientific animation.

From 1985 to 1989, Jones was the Director of Engineering Animation at Failure Analysis Associates, the largest private U.S. engineering and scientific services consulting firm. While at FaAA, Jones produced more than 30 engineering animations, comprising more than five hours of computer graphics animation. Prior to 1985, Jones was a Research Associate at Brigham Young University's Engineering Computer Graphics Laboratory. He conducted research and development of high-performance graphics devices and state-of-the-art computer graphics software. He is the principal author of DYNAMOVIE.BYU.

Jones received his Ph.D. in engineering at Brigham Young University in 1985. He is a member of the American Society of Mechanical Engineers, the Association of Computing Machines - SIGGRAPH, and the National Computer Graphics Association. Jones also is an associate member of the Institute

of Electrical and Electronic Engineers. During 1992, he was an invited speaker at the DOE Computer Graphics Forum and the International AVS Workshop. Currently he is serving as the chairman of both the SIG on Scientific Visualization at Hanford and the local ACM-SIGGRAPH chapter. Also, he is a member of the steering committee for the DOE Computer Graphics Forum and a member of SLATEC. He has written or contributed to more than a dozen publications in his field.

Dr. Richard J. Kouzes is a Staff Scientist in the MSRC Computing and Information Sciences program and leader of the Computer Instrumentation and Electronics group, which is conducting experimental research in advanced data acquisition system development and precision atomic mass measurements using FTICR. Kouzes' work includes computer modeling of physical systems to enhance instrument performance so that atomic masses can be measured to higher precision.

Prior to joining PNL, Kouzes was a Senior Research Physicist and Lecturer at Princeton University. While at Princeton, he collaborated in two major international solar neutrino experiments, actively pursued research in nuclear techniques for precision atomic mass measurements, and developed several data acquisition systems for nuclear physics applications.

Kouzes earned his Ph.D. in physics from Princeton University in 1974 under the direction of Professor Rubby Sherr. At Princeton, he built one of the highest-resolution magnetic spectrometers available for nuclear structure research and made a precise measurement of the mass of ^8He . He also developed particle detectors and a data acquisition system for spectroscopic applications.

Kouzes did postdoctoral work at The Indiana University, where he assembled the magnetic spectrometer system and developed the data acquisition system used for the University's Cyclotron Facility. He is a leader in the field of computerized data acquisition and was a founder and past chairman of the IEEE Computer Applications in Nuclear and Plasma Sciences Committee. He is the author of more than 60 papers.

Mr. Richard J. Littlefield leads the Computing and Information Sciences program in High Performance Computing. His current research interests target massively parallel computing for scientific

applications and focus on performance modeling and evaluation, algorithm selection, software structure and development tools, and numerical methods. Littlefield's prior work includes the design and construction of several custom parallel computers for image analysis, visualization, and reconstruction of solids scanned with ultrasound using the synthetic aperture focusing technique.

Littlefield has more than 20 years experience in computing, spanning a spectrum from development and support of production software and hardware through research publications. He received his M.S. in computer science and B.S. in mathematics from the University of Washington. Littlefield holds one patent and has authored more than 25 papers in the areas of parallel computing, analysis of large data sets, computer graphics, and image processing. He is a member of the IEEE Computer Society, ACM, and Society of Industrial and Applied Mathematics.

Mr. Thomas J. Mathieu, a scientist, joined PNL in 1977. He is currently the group leader for the MSRC/EMSL Computer Support Group and is assigned through the Information Systems and Services Directorate. Prior to this assignment, Mathieu managed the IS&S Integrated Computing Environment Service Center. He also held various system programming, system administration, and team leader positions at PNL.

Mathieu received his M.S. from the State University of New York at Buffalo in 1976 and his B.S. degree in applied mathematics and computer science from Brown University in 1969. He is an instructor at Washington State University/Tri-Cities, where he has taught computer science classes for the past 15 years.

Mr. David R. McGee, is an Information Systems Specialist with the MSRC's Computing and Information Sciences program. He joined PNL in 1983 and has nine years experience working with information systems. McGee currently is responsible for personal computing for more than 200 Macintosh and DOS Windows-based systems used by MSRC staff. In addition, he is contributing to the design and installation of the computing infrastructure of the Environmental and Molecular Sciences Laboratory.

McGee has made presentations and moderated sessions at computing conferences such as MacWorld

and SEAM and is the co-author of a scientific publication on an object-oriented analysis of research chemistry. He is experienced in the use of computer languages such as C++, C, Pascal, Modula-2, Basic, and Fortran as well as operating systems such as UNIX, VMS, MacOS, DOS, and MS Windows. He is currently taking courses in computer science (with emphasis on engineering) at Washington State University/Tri-Cities, and he attended the University of Washington in Seattle from 1984 to 1986.

Mr. Marty J. Peterson is a Senior Development Engineer with PNL's Applied Physics Center. Currently he is part of the Systems Engineering Group of the MSRC Computing and Information Sciences program. In this capacity, Peterson is task leader and principal investigator for the design and prototyping of networks to support a large computational-intensive laboratory. Technologies being prototyped/evaluated include FDDI, HiPPI, Fibre Channel, ATM, with an emphasis on optimization of routed subnetworks and placement of key resources.

Peterson's work is focused on designing a flexible, high-speed hierarchy of networks supporting massively parallel supercomputers, high-speed network file server resources, and office workstations. Applications to be supported include computational chemistry codes, large experimental data sets, and graphics and visualization.

Peterson has a strong background in communications design of local area networks, Network Operating Systems, protocols, microwave radio communications, fiber optics technologies, and project management skills. He is a Professional Licensed Electrical Engineer in the state of Washington and is active in the local Institute of Electrical and Electronic Engineers, Siggraph/SigCom, and Professional Engineering societies.

Mr. Bill J. Pitre, a research scientist, joined PNL in 1989. He is assigned to the EMSL/MSRC Project Support Group through the Laboratory's Information Systems and Services Directorate. Pitre provides dedicated support for the MSRC's UNIX workstations. He earned his B.S. degree in computer science at California State University in Dominguez Hills in 1986.

Mr. James Schroeder is a staff engineer with PNL's Applied Physics Center and is currently assigned to

the MSRC Computing and Information Sciences program. He leads the Distributed Computing Systems activities for the program. His current technical focus is the integration of diverse computing technologies and resources to meet operational and performance requirements in a timely and cost-effective manner. Schroeder's work experience includes development of real time control and data collection systems for laboratory, field, and remote sensing applications, data collection and analysis systems for manufacturing industries, system-level software development, and project management. Schroeder earned an M.S. in Electrical Engineering from the University of New Mexico in 1973. His publications are in the areas of distributed data systems and shop floor information systems.

Mr. Geoffrey S. Slinker is a member of the Computing and Information Sciences program working in the areas of scientific visualization, graphical user interfaces, and software engineering guidelines. His current research interests include configuration management, user interface management systems, photo-realistic rendering, and computer animation.

Slinker has recently graduated from Brigham Young University, receiving both his B.S. and M.S. in computer science and was a member of Phi Kappa Phi. Slinker has one publication in the Journal of Imaging Science and Technology, and has been cited for unpublished work in several journals including the 1993 proceedings of SIGGRAPH.

Mr. Kerry D. Steele, a Senior Research Engineer in PNL's Applied Physics Center, is assigned to the MSRC Computing and Information Sciences program. Since joining PNL in 1984, Steele has specialized in the areas of microcomputer data acquisition and control systems, data communications, and information management systems.

In his work with the Applied Physics Center, Steele managed the specification and design of a Command Control Communications and Intelligence system; conceived and led the development of a microprocessor-based interface that links battlefield reporting systems with information management systems; designed and developed communications software for a multinode integrated network of graphics workstations; and developed software for data acquisition systems for vitrification systems that process contaminated soil. Prior to 1984, Steele served 20 years

in the United States Navy, progressing from enlisted technician to commissioned officer. He received his B.S. in electrical engineering from Washington State University in 1984 and has completed graduate-level courses in electrical engineering at WSU.

Mr. Gregory S. Thomas joined PNL in 1991 and is a Research Scientist with the MSRC's Computing and Information Sciences program. His primary interests include computer graphics, user interfaces, and high-performance parallel computing. He is the lead developer of the user interface for GnomeView, an integrated graphical interface to several genomic databases.

In addition, Thomas is working on several projects related to the computing capabilities in the Environmental and Molecular Sciences Laboratory. He is facilitating interchangeability of performance visualization tools for parallel programs. He has developed software that translates program trace data from one tool's format to another. He has modified various existing visualization tools to enhance their capabilities in several areas (e.g., critical path analysis). He also is developing a benchmark suite to be used in the acquisition of a parallel supercomputer.

Prior to joining PNL, Thomas spent three years as a research assistant in the Computer Science Department at the University of Washington, where he performed original theoretical, design, implementation, and performance analysis work to extend the domain of parallel simulation to include Petri nets. He designed and developed xsim, an interactive X11 application that is dynamically configurable as a uniform graphical interface for a variety of simulation and analysis tools.

Thomas received his M.S. in computer science from the University of Washington in 1991 and his B.A. in computer science and statistics from the University of California at Berkeley in 1988. During his academic career he earned the following honors: Phi Beta Kappa, Golden Key National Honor Society, High Distinction in General Scholarship, High Honors in Computer Science, High Honors in Statistics, Chancellor's Scholar, and Alumni Scholar. He has written or contributed to several publications in his field.

Mr. Erin N. Thornton is a Research Scientist with the MSRC's Computing and Information Sciences

program. His interests include computer graphics applications to science, especially in visualizing scientific data, and in using computer graphics in education (e.g., for internal education such as peer-to-peer communication). He joined PNL in 1990 after receiving his M.S. and B.S. (*Cum Laude*) degrees in engineering from Brigham Young University, where he was a member of the Tau Beta Phi Engineering Honor Society and Outstanding Civil Engineering student for 1990.

Thornton developed the crystallographic modeling and visualization system called SPACE. In 1992, this advanced visualization system (AVS) application was presented at the Department of Energy's Computer Graphics Forum in Gatlinburg, Tennessee, and at the First International AVS User Group Conference in Research Triangle Park, North Carolina.

Mr. Eugene W. Wallace, a Senior Technician with the MSRC's Computing and Information Sciences program, works on mechanical and electronic fabrication projects. He joined PNL in 1965, and was a member of the team that built the "Amazing Micromouse," a maze-solving robot that won an international competition. During his career at PNL, Wallace also provided hardware support to a large project conducted for the U.S. Army and worked on a radiation detection device that is now carried in all U.S. space shuttles. In addition to his work for the MSRC and the Environmental and Molecular Sciences Laboratory, Wallace does general electronic and mechanical fabrication for PNL's Computer Sciences Department.

Prior to joining PNL, Wallace spent 10 years in experimental nuclear physics with General Electric. During this period, he worked on the Vernier Chronotron, the world's fastest timing device during that time, with the resolution of 1/10th of a nanosecond. He also contributed several innovative ideas while measuring the "total neutron cross section of all the elements and separated isotopes available."

MSRC Associates

Dr. James L. Anchell

Postdoctoral Appointee - Theory, Modeling, and Simulation

Postdoctoral Fellow, Institute for Molecular Science, Okazaki, Japan, 1991-1992 (advisor: Professor Keiji Morokuma); Postdoctoral Fellow, University of Utah,

1989-1991 (advisor: Professor Jack Simons); Ph.D., Physical Chemistry, University of Wisconsin, 1989; B.S. Chemistry and B.A. Mathematics, Humboldt State University, 1983.

Dr. Gregory E. Arnold

Postdoctoral Appointee - Theory, Modeling, and Simulation

Ph.D., Biochemistry, Washington State University, 1989 (advisor: Dr. A. Keith Dunker); M.S., Chemistry, Washington State University, 1986; B.S., Chemistry, University of Oregon, 1984.

Dr. David L. Blanchard

Postdoctoral Appointee - Materials and Interfaces

Ph.D., Chemistry, University of Washington, 1989 (advisor: Tom Engel); B.A., Chemistry, Johns Hopkins University, 1983.

Dr. Kirk W. Brown

Postdoctoral Appointee - Chemical Structure and Dynamics

Ph.D., Physical Chemistry, Oregon State, 1991 (advisor: Joseph Nibler); B.S., Chemistry, Idaho State University, 1987.

Dr. Lloyd A. Bumm

Postdoctoral Appointee - Chemical Structure and Dynamics

Postdoctoral Fellow, physics, IBM Zurich Research Laboratory, 1989-1990 (advisor: D. Pohl); Ph.D., Physical Chemistry, Northwestern University, 1991 (advisor: R. P. Van Duyne); M.S., Physical Chemistry, Northwestern University, 1983; B.S., Chemistry, Clarkson University, 1982.

Dr. Ellen L. Chappell

Postdoctoral Appointee - Chemical Structure and Dynamics

Postdoctoral Fellow, Chemical Physics Laboratory at SRI International 1990-91 (advisor: David Crosley); Ph.D., Physical Chemistry, University of Oregon, 1990 (advisor: Paul Engelking); B.S., Evergreen State College, 1985.

Dr. Thomas J. Godin

Postdoctoral Appointee - Theory, Modeling, and Simulation

Research Associate, Department of Physics, University of Oregon, 1989-90; Assistant Professor of Physics, University of Portland, 1988-89; Ph.D., Physics, University of Oregon, 1988; M.S., Physics, University of Oregon, 1984; B.S., Mathematics, University of Rhode Island, 1982.

Dr. Gregory S. Herman

Postdoctoral Appointee - Materials and Interfaces

Ph.D., Chemistry, University of Hawaii, 1992 (advisor: Dr. Charles S. Fadley); B.S., Chemistry, University of Wisconsin, Parkside, 1985.

Dr. Albert T. Hu

Postdoctoral Appointee - Chemical Structure and Dynamics

Postdoctoral Fellow, University of Rochester 1989-91 (advisor: John S. Muentner); Ph.D., Chemical Physics, University of Oregon, 1989.

Dr. John E. Jaffee

Senior Research Fellow - Theory, Modeling, and Simulation

Assistant Professor, Department of Physics, Michigan Technological University, 1985-1992; Postdoctoral Associate, Department of Physics, State University of New York at Stony Brook, 1983-1985 (advisor: P. B. Allen); Postdoctoral Research Associate, Solar Energy Research Institute, 1981-1983 (advisor: A. Zunger); Ph.D., Physics, Cornell University, 1982 (advisor: N. W. Ashcroft); M.S., Physics, University of Illinois, Urbana-Champaign, 1976; B.A., *Cum Laude*, Physics, Cornell University, 1974.

Dr. Alan G. Joly

NORCUS Postdoctoral Fellow - Chemical Dynamics and Structure

Ph.D., Chemistry, Massachusetts Institute of Technology, 1990 (advisor: Keith Nelson); B.S., Chemistry, University of Rochester, 1985.

Dr. Michael A. Kennedy

Alexander Hollaender Postdoctoral Fellow - Macromolecular Structure and Dynamics

Ph.D., Physical Chemistry, University of South Carolina - Columbia, 1989; B.S., Chemistry, Muskingum College, 1984.

Dr. Richard D. Knochenmuss

Senior Research Fellow - Chemical Structure and Dynamics

Staff Scientist, Paul Scherer Institute, Villigen, Switzerland, 1990-91; Postdoctoral Fellow, University of Bern, Switzerland, 1984-89, with Profs. H. Guedel and S. Leutwyler; Ph.D., Washington State University, 1984.

Mr. Mlu Kwini

Graduate Student - Chemical Dynamics and Structure

Ph.D. Candidate (1992), Physical Chemistry, University of California-Santa Barbara.

Dr. Brian L. Maschhoff

Postdoctoral Appointee - Chemical Structure and Dynamics

Postdoctoral Fellow, Rutgers University, 1988-91, with Professor Theodore Madey; Ph.D., Chemistry, University of Arizona, 1988 (Advisor: Professor Neal Armstrong); B.S., Chemistry, University of New Mexico, 1981.

Dr. Michael Messina

Postdoctoral Appointee - Theory, Modeling, and Simulation

Ph.D., Chemistry, University of Pittsburgh, 1992 (advisor: Professor R. D. Coalson); B.S., Chemistry, State University of New York at Stony Brook, 1987; A.S., Chemistry, Nassau Community College, 1985.

Dr. Mark D. Paulsen

Postdoctoral Appointee - Theory, Modeling, and Simulation

Ph.D., Physical Chemistry, University of Wisconsin-Madison, 1989 (advisor: M. Thomas Record); B.S., Chemistry, University of Nebraska-Lincoln, 1982.

Dr. Kirk A. Peterson

Postdoctoral Appointee - Theory, Modeling, and Simulation

Postdoctoral Fellow, Universitt Bielefeld, FRG, 1990-1992 (advisor: H.-J. Werner); Ph.D., Chemistry, University of Wisconsin-Madison, 1990 (advisor: R. Claude Woods); B.S., Chemistry, Seattle University, 1983.

Dr. Ronald D. Poshusta

Visiting Scientist - Theory Modeling, and Simulation

Professor of Chemistry, Washington State University. WSU Chemistry faculty since 1967; Ph.D., Chemistry, University of Texas, 1963 (mentor: F. A. Matsen); B.S., Iowa State University, 1957.

Dr. Steven P. Sapers

Postdoctoral Appointee - Chemical Structure and Dynamics

Postdoctoral Fellow, Physical Chemistry, University of Toronto, 1990-1991 (advisor: James Donaldson); Ph.D., Physical Chemistry, University of Colorado, 1989 (advisor: Veronica Vaida); B.A., Chemistry, Brandeis University, 1984.

Dr. David E. Smith

Postdoctoral Appointee - Theory, Modeling, and Simulation

Postdoctoral Fellow, University of Sydney, Australia, 1991-1992 (advisor: A.D.J. Haymet); Postdoctoral Fellow, University of Utah, 1989-1991 (advisor: A.D.J. Haymet); Ph.D., Physical Chemistry, University of California-Berkeley, 1989; B.A., Chemistry, Colorado College, 1984.

Dr. Scott Smith

Postdoctoral Appointee - Chemical Dynamics and Structure

Ph.D., Chemistry, University of Utah, 1988; B.S., Chemistry, Northern Arizona University, 1983.

Dr. Mark S. Stave

Postdoctoral Appointee - Molecular Science Software

Ph.D., Chemistry, Iowa State University, 1991 (advisor: A.E. DePristo); B.A., Chemistry, St. Olaf College, 1986.

Dr. Thuy T. Tran

Postdoctoral Appointee - Materials and Interfaces

Ph.D., Chemistry, University of Hawaii, 1992 (advisor: Dr. Charles S. Fadley); B.A. Chemistry, Williams College, 1984 (advisor: Dr. William R. Moomaw)

Dr. Mark O. Trulson

Postdoctoral Appointee - Chemical Dynamics and Structure

National Institutes of Health Fellow, Massachusetts Institute of Technology, 1988-1989 (advisor: Keith Nelson); Ph.D., Chemistry, University of California-Berkeley, 1987 (advisor: Richard Mathies); B.S., Chemistry, Arizona State University, 1981.

Dr. Julia C. White

Postdoctoral Appointee - Theory, Modeling, and Simulation

Ph.D., Chemistry, Indiana University, 1991 (advisor: Ernest Davidson); B.A., Chemistry, Earlham College, 1986.

Dr. David E. Woon

Postdoctoral Appointee - Theory, Modeling, and Simulation

Postdoctoral Fellow, University of Texas at Arlington, 1990-1991 (advisor: Dennis S. Marynick); Ph.D., Metallurgy, Michigan Technological University, 1989 (advisor: Donald R. Beck); M.S., Physics, MTU, 1987; B.S., Metallurgy, MTU, 1984.

Appendix B

1992 Publications and Presentations

Appendix B

1992 Publications and Presentations

Publications

- Anderson, S. L., A. K. Datye, E. J. Braunschweig, and C. H. F. Peden, "Reactivity of Novel Ion-Exchanged Nickel/Hydrous Titanate Catalysts," *Appl. Catal. A*, **82**:185 (1992).
- Andrade, J. D., V. Hlady, A-P. Wei, C-H. Ho, A. S. Lea, S. I. Jeon, Y. S. Lin, and E. Stroup, "Proteins at Interfaces: Principles, Multivariate Aspects, Protein Resistant Surface, and Direct Imaging and Manipulation of Adsorbed Proteins," *Clinical Materials*, **11**:67-84 (1992).
- Arnold, G. E., L. A. Day, and A. K. Dunker, "Tryptophan Contributions to the Unusual Circular Dichroism of fd Bacteriophage," *Biochemistry*, **31**, **34**:7948 (1992).
- Arnold, G. E., A. K. Dunker, S. J. Johns, and R. J. Douthart, "Use of Conditional Probabilities for Determining Relationships Between Amino Acid Sequence and Protein Secondary Structure," *PROTEINS: Structure, Function, and Genetics*, **12**:382 (1992).
- Arnold, G. E., and R. L. Ornstein, "A Molecular Dynamics Simulation of Bacteriophage T4 Lysozyme," *Protein Engineering*, **5**:703 (1992).
- Baer, D. R., "Chemical Properties," Chapter 3 of *Characterization of Metals and Alloys* (Ed. P. Holloway), in: *Practical Guides for the Surface, Interfacial and Microanalysis of Materials* (Eds. C. R. Brundle and C. Evans), pp. 24-50. Butterworth Press, Stoneham, Massachusetts (1992).
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- Baer, D. R., C. W. Hubbard, and R. L. Gordon, "Pd, Ni and Cu Overlayers on Polycrystalline Re," *J. Vac. Sci. Technol.*, **A10**:2391 (1992).
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- Baer, D. R., C. F. Windisch Jr., and R. H. Jones, "Application of Combined Surface Analysis/Corrosion Cell Experiments to Stress Corrosion Cracking Research," in: *Parkins Symposium on Fundamental Aspects of Stress Corrosion Cracking* (Ed. S. M. Bruemmer), p. 511. The Minerals, Metals and Materials Society, Warrendale, Pennsylvania (1992).
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- Bair, R. A., M. A. Thompson, R. J. Littlefield, R. A. Kendall, and T. H. Dunning, Jr., "PNL Scientists Gear Up to Solve Environmental Problems," *CSCC Update*, **13**(2) (1992).
- Ballinger, T. H., R. S. Smith, S. D. Colson, and J. T. Yates, Jr., "Thermal Decomposition of 1,1,1-Trichloroethane and 1,1-Dichloroethene over High Surface Area Alumina," *Langmuir*, **8**:2408 (1992).
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Chambers, S. A., "Elastic Scattering and Interference of Backscattered Primary, Auger, and X-ray Photoelectrons at High Kinetic Energy: Principles and Applications," *Surface Science Reports*, **16**:261-332 (1992).

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- Edmonds, C. G., A. L. Fuciarelli, and D. L. Springer, "Electrospray Ionization Mass Spectrometry for Natural and Radiation Induced Modifications in Histone Proteins," presented at the 40th ASMS Conference on MS and Allied Topics, Washington, D.C., May 31-June 5, 1992.
- Edmonds, C. G., J. A. Loo, R. D. Smith, A. F. Fuciarelli, B. T. Thrall, J. D. Morris, and D. L. Springer, "Evaluation of Histone Sequence and Modifications by Electrospray Ionization Mass Spectrometry and Tandem Mass Spectrometry," presented at the Hanford Life Sciences Symposium, Richland, Washington, October 10-22, 1992.
- Edmonds, C. G., J. A. Loo, R. D. Smith, A. F. Fuciarelli, B. T. Thrall, J. D. Morris, and D. L. Springer, "Evaluation of Histone Sequence and Modifications by Electrospray Ionization Mass Spectrometry and Tandem Mass Spectrometry," presented at the Pacific Conference on Chemistry and Spectroscopy, Foster City, California, October 21, 1992.
- Edmonds, C. G., J. C. Schwartz, I. Jardine, "Peptide Sequencing by Quadrupole Ion Trap Mass Spectrometry," presented at the 40th ASMS Conference on MS and Allied Topics, Washington, D.C., May 31-June 5, 1992.
- Edmonds, C. G., D. L. Springer, D. M. Sylvester, S. C. Goheen, and R. J. Bull, "Characterization of Acrylamide Adducted Hemoglobin and Proteolytically-Derived Peptides Based on Electrospray Ionization Mass Spectrometry," presented at the 40th ASMS Conference on MS and Allied Topics, Washington, D.C., May 31-June 5, 1992.
- Ermler, W. C., and M. M. Marino. "Ab Initio Configuration Interaction Studies of Cs_2 , Cs_2^+ , and $\text{Cs}(\text{H}_2\text{O})^+$." West Coast Theoretical Chemistry Conference, Richland, Washington, May 21-23, 1992.
- Feller, D. F. "Application of Systematic Sequences of Wavefunctions to Studies of Hydrogen Bonding." 1992 West Coast Theoretical Chemistry Conference, Richland, Washington, May 21-23, 1992.
- Feyereisen, M. W. and R. A. Kendall. "An Implementation of the Computational Chemistry Program DISCO on the Delta." First Intel Delta Applications Workshop, Pasadena, California, February 11-12, 1992.
- Gibson, A. S., R. Haydock, and J. P. LaFemina, "Electronic Structure of Neutral and Charged Vacancy Defects in Periclase," presented at the Environmental Interfaces Topical Conference, 39th Annual Symposium of the American Vacuum Society, Chicago, Illinois, November 9-13, 1992.
- Gibson, A. S., R. Haydock, and J. P. LaFemina, "Electronic Structure of Oxygen Vacancy Defects in MgO ," presented at the 1992 Meeting of the American Physical Society, Indianapolis, Indiana, March 16-20, 1992.
- Gibson, A. S., R. Haydock, and J. P. LaFemina, "Electronic Structure of Vacancy and Surface Vacancy Defects in MgO Crystals," presented at the 1992 Spring Meeting of the Materials Research Society, San Francisco, California, April 27-May 1, 1992.
- Gibson, A. S., R. Haydock, and J. P. LaFemina, "The Electronic Structure of Bulk and Surface Oxygen Vacancy Defects in Periclase," presented at the 13th Annual West Coast Theoretical Chemistry Conference, Richland, Washington, May 21-23, 1992.
- Godin, T. J., "Atomic Structure of the SnO_2 (110) Surface," presented at the Oregon Materials Science Symposium, Corvallis, Oregon, May 9, 1992.

Godin, T. J., and J. P. LaFemina, "Application of Tight-Binding, Total-Energy Techniques to Mineral Oxide Surface Atomic Structures," presented at the Fall 1992 Meeting of the American Geophysical Union, San Francisco, California, December 7-11, 1992.

Godin, T. J. and J. P. LaFemina. "New Tight-Binding Model for Mineral Oxide Surfaces: Surface Structure of Tridymite and Cristobalite." American Geophysical Union Spring Meeting, Montreal, Canada, May 12-15, 1992.

Godin, T. J. and J. P. LaFemina. "New Tight-Binding Pair Potentials for Mineral Oxides: Application to Cassiterite (110) β -Tridymite (1010) and β -Cristobalite (110)." Materials Research Society Spring Meeting, San Francisco, California, April 26-30, 1992.

Goodlett, D. R., J. H. Wahl, H. R. Udseth, and R. D. Smith, "CE/ESI-MS in Small (<20 μ m) Diameter Capillaries," presented at the 40th ASMS Conference on MS and Allied Topics, Washington, D.C., May 31-June 5, 1992.

Goodlett, D. R., J. H. Wahl, H. R. Udseth, and R. D. Smith, "Use of CE/ESI-MS to Investigate Solution and Gas Phase Protein Conformation," presented at the 40th ASMS Conference on MS and Allied Topics, Washington, D.C., May 31-June 5, 1992.

Grate, J. W., "Solvent Effects on the Decarboxylation of 3-Carboxybenzisoxazole Ions: Cavity Effects and Relevance to Catalysis by an Antibody," presented at the Meeting on Solute/Solvent Interactions, Aberdeen Proving Ground, Maryland, May 27-29, 1992.

Grate, J. W., R. A. McGill, and M. H. Abraham, "Chemically Selective Polymer Coatings for Acoustic Vapor Sensors and Arrays," presented at the 1992 IEEE Ultrasonics Symposium, Tucson, Arizona, October 20-23, 1992.

Grate, J. W., R. A. McGill, and M. H. Abraham, "Polymer-Coated Surface Acoustic Wave Vapor Sensors Respond to Swelling-Induced Modulus Changes," presented at the 182nd Meeting of The Electrochemical Society, Toronto, Ontario, Canada, October 11-16, 1992.

Grate, J. W., S. W. Wenzel, and R. M. White, "Sensing Transition Behaviors in Polymer Thin Films on Flexural Plate Wave Devices," presented at the 203rd American Chemical Society National Meeting, San Francisco, California, April 5-10, 1992.

Harrison, R. J. "Ab Initio Chemistry in Parallel." German Theoretical Chemistry Conference, Max Planck Institute, Brixen, Austria, September 24-30, 1992.

Harrison, R. J. "Real Time Visualization of Quantum Molecular Dynamics." Supercomputing '92, Minneapolis, Minnesota, November 16-20, 1992.

Hess, A. C. "Ab Initio Periodic Hartree-Fock Theory: Applications in Geochemistry and Mineralogy." American Geophysical Union Spring Meeting, Montreal, Canada, May 12-15, 1992.

Hess, A. C., and M. I. McCarthy. "A Theoretical Study of the Chemistry and Physics of Clay Surfaces: Comparison of Kaolinite, Pyrophyllite, and Talc using Periodic Hartree-Fock Theory." 1992 American Geophysical Union Fall Meeting, San Francisco, California, December 7-11, 1992, San Francisco, California.

Hess, A. C., and J. C. White. "Periodic Hartree-Fock Theory in Zeolite Catalysis: Prospects and Perspectives." 1992 American Chemical Society National Meeting, San Francisco, California, April 5-10, 1992.

Hess, W. P., "Photodissociation Study of $\text{BrCH}_2\text{CH}_2\text{OH}$ and $\text{ICH}_2\text{CH}_2\text{OH}$: Formation and Characterization of OH ($X^2\Pi$)," presented at the American Chemical Society National Meeting, San Francisco, California, April 1992.

Hess, W. P., "Programs at the Molecular Science Research Center and Environmental Restoration at the Hanford Site," presented at the Sandia National Laboratory Symposium, Albuquerque, New Mexico, June 1992.

Hess, W. P., "Two-Step Photodissociation of Bromoethanol by Photofragment Imaging and Laser-Induced Fluorescence," presented at the Washington State University Physics Colloquium, Pullman, Washington, September 1992.

- Hu, T. A., E. L. Chappell, and S. W. Sharpe, "Observation of the Weakly Bonded Ar-N₂O Complex in the 2256 cm⁻¹ Combination Region: The Intermolecular Bend or Stretch?" presented at the Ohio State University International Symposium on Molecular Spectroscopy, Columbus, Ohio, June 15-19, 1992.
- Iwamiya, J. H., S. W. Sinton, J. Callahan, and G. P. Drobný, "Application of Optimal Control Theory in Solid State NMR: Time Suspension Pulse Sequences," presented at the 33rd Annual ENC, The Asilomar Conference Center, Pacific Grove, California, 1992.
- Jaffee, J. E. "High-Pressure Properties of ZnS and ZnO by *Ab Initio* Hartree-Fock Theory." 1992 American Geophysical Union Fall Meeting, San Francisco, California, December 7-11, 1992.
- Janata, J., "Analytical Use of Work Function," presented at the Washington State University, Pullman, Washington, March 1992.
- Janata, J., "Analytical Use of Work Function," presented at the Int. Conf. on Metallurgical Coatings, San Diego, California, April 1992.
- Janata, J., "Analytical Use of Work Function," presented at the Fritz-Haber-Institute, Berlin, Germany, October 1992.
- Janata, J., "Chemical Modulation of Work Function in Chemical Sensors," presented at the Fritz-Haber Institute, Berlin, Germany, October 1992.
- Janata, J., "Chemical Microsensors in Environmental Monitoring," presented at the 25th Heyrovsky Discussions Meeting, Prague, Czechoslovakia, June 1992.
- Janata, J., "Environmental Electrochemical Sensors," presented at the 25th Heyrovsky Discussion Meeting, Prague, Czechoslovakia, June 1992.
- Janata, J., "Environmental Sensors," presented at the Microsystems Int. Conference, Berlin, Germany, October 1992.
- Janata, J., "Fabrication of Chemical Sensors," presented at the Royal Society of Chemistry Autumn Meeting, Dublin, Ireland, September 1992.
- Janata, J., "Ion Optodes," presented at the Technical University, München, Weihenstephan, Germany, June 1992.
- Janata, J., "Ion Optodes," presented at the Dublin Institute of Technology, Dublin, Ireland, September 1992.
- Janata, J., "Microfabricated Electrochemical Sensors for Gas Sensing," presented at the Royal Society of Chemistry Meeting, Dublin, Ireland, September 1992.
- Janata, J., "Organic Films in Field-Effect Transistor Sensors," presented at the Gordon Research Conference, Ventura, California, February 1992.
- Janata, J., "Organic Semiconductors as Sensing Materials," presented at the 39th National Symposium Topical Conference of the American Vacuum Society, Chicago, Illinois, November 9-13, 1992.
- Janata, J., "Solid State Sensor for HCN," presented at the BMFT Meeting, Duisburg, Germany, June 1992.
- Janata, J., "Towards Artificial Nose," submitted in the Science Pour L'Art contest, Paris, France, February 1992.
- Jones, D. R., and E. N. Thornton. "Visualizing Crystals with AVS SPACE Viewer Beta Version 1.0." First International AVS User Group Conference, North Carolina, February 11-13, 1992.
- Joyce, S. A., "Force Microscopy Studies of Interfacial Phenomena," presented at the Washington State University Physics Colloquium, Pullman, Washington, March 12, 1992.
- Kay, B. D., "Quantum-Resolved Inelastic and Reactive Gas-Surface Scattering," presented at the Physical Chemistry Seminar, University of Washington, Seattle Washington, May 28, 1992.

Kay, B. D., "Quantum-Resolved Inelastic and Reactive Gas-Surface Scattering," presented at the Air Force Phillips Laboratory, Hanscomb Air Force Base, Massachusetts, July 18, 1992.

Kay, B. D., "Quantum-Resolved Inelastic and Reactive Molecular Beam Scattering from Surfaces," presented at the Physical Chemistry Seminar, Oklahoma State University, Stillwater, Oklahoma, July 27, 1992.

Kay, B. D., "Quantum-Resolved Inelastic and Reactive Gas-Surface Scattering," presented at the Surface Science Seminar, Naval Research Laboratory, Washington, D.C., August 31, 1992.

Kay, B. D., "State-to-State Dynamics of Inelastic N₂ Molecular Beam Scattering from Au(111), Pd(111), and Pd(111):H," presented at the Gordon Conference on Atomic and Molecular Interactions, New London, New Hampshire, July 20-24, 1992.

Kay, B. D., "Surface Kinetics of H/D Exchange on Pd(111): A Steady-State Molecular Beam Study," presented at the Gordon Conference on Atomic and Molecular Interactions, New London, New Hampshire, July 20-24, 1992.

Kendall, R. A., and R. A. Bair. "Initial Experiences with the Intel Touchstone Delta Parallel Computer System." First Intel Delta Applications Workshop, Pasadena, California, February 11-12, 1992.

Kennedy, M. A., "DNA Structure and Dynamics Using NMR Spectroscopy," presented at the U.S. Department of Energy 25th Radiological and Chemical Physics Contractor's Meeting, Wakulla Springs Lodge and Conference Center, Wakulla Springs, Florida, June 1992.

Kennedy, M. A., "Evidence for a Mobile Base at the T-A Junction in a T₃-A₃ Containing DNA Oligomer," presented at the 11th Meeting of the International Society of Magnetic Resonance, University of British Columbia, Vancouver, B.C., July 1992.

Kouzes, R. T. "Fourier Transform Ion Cyclotron Resonance Precision Atomic Mass Measurement Limits." Sixth International Conference on Nuclei Far From Stability and the Ninth International Conference on Atomic Masses and Fundamental Constants, Bernkastel-Kues, Germany, July 19-24, 1992.

LaFemina, J. P., A. M. Bowler, J. C. Hermanson, and C. B. Duke, "Surface Atomic Structure and Bonding of GaAs(110)-p(1x1)-Bi(1ML)," presented at the 19th Annual Conference on the Physics and Chemistry of Semiconductor Interfaces, Death Valley, California, January 28-30, 1992.

LaFemina, J. P., A. M. Bowler, J. C. Hermanson, C. B. Duke, "Tight-Binding, Total-Energy Computations of the Surface Atomic and Electronic Structure of the GaAs (110)-p(1x1)-Bi Interface," presented at the 19th Conference on Physics and Chemistry of Semiconductor Interfaces, Death Valley, California, January 28-30, 1992.

LaFemina, J. P., A. S. Gibson, and R. Haydock, "Bulk and Surface Oxygen Vacancy Defects in Periclase (MgO)," presented at the American Vacuum Society Pacific Northwest Chapter Richland Symposium, Richland, Washington, September 10-11, 1992.

LaFemina, J. P., A. Gibson, and R. Haydock, "Electronic Structure of Neutral and Charged Surface Vacancy Defects in Periclase," presented at the 39th Annual American Vacuum Society Meeting, Chicago, Illinois, November 9-13, 1992.

LaFemina, J. P., A. Gibson, and R. Haydock, "Electronic Structure of Oxygen Vacancy Defects in MgO," presented at the 1992 March Meeting of the American Physical Society, Indianapolis, Indiana, March 1992.

LaFemina, J. P., A. Gibson, and R. Haydock, "Electronic Structure of Vacancy and Surface Vacancy Defects in MgO Crystals," presented at the 1992 Spring Materials Research Society Meeting, San Francisco, California, April 1992.

LaFemina, J. P., and S. A. Kafafi, "Electronic Structure and Photophysical Properties of Aromatic Polyimides," presented at the 13th Annual West Coast Theoretical Chemistry Conference, Richland, Washington, May 21-23, 1992.

LaFemina, J. P., and S. A. Kafafi, "Electronic Structure and Photophysical Properties of Polyimides," presented at the Spring 1992 American Chemical Society Meeting, San Francisco, California, April 1992.

LaFemina, J. P., and S. A. Kafafi, "Photophysical Properties and Intramolecular Charge Transfer in Aromatic Polyimides," presented at the 203rd American Chemical Society National Meeting, San Francisco, California, April 5-10, 1992.

Lessor, D. L., C. B. Duke, and K. F. Canter, "Low Energy Electron and Positron Diffraction. What You Learn. How they Differ," presented at the Fifth International Workshop on Slow-Positron Beam Techniques for Solids and Surfaces, Jackson, Wyoming, August 6-10, 1992.

Lessor, D., L., C. B. Duke, A. Paton, and A. Kahn, "Surface Bondlengths for Zincblende Structure Semiconductor (110) Surfaces from Low Energy Electron Diffraction Using a Gradient Search," presented at the 1992 West Coast Theoretical Chemistry Conference, Richland, Washington, May 20-22, 1992.

Lessor, D. L., C. G. Duke, A. Paton, W. K. Ford, S. M. Chen, G. R. Brandes, and K. F. Canter, "LEPD Study of GaAs (110) and InP (110) Surfaces," presented at 1992 March Meeting of the American Physical Society, Indianapolis, Indiana, March 1992.

Light-Wahl, K. J., B. E. Winger, J. A. Loo, M. Busman, A. L. Rockwood, and R. D. Smith, "The Use of Electrospray Ionization Mass Spectrometry and Tandem Mass Spectrometry to Gain Insight into Protein Structure," presented at the 43rd Pittsburgh Conference & Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, Louisiana, March 9-13, 1992.

Light-Wahl, K. J., B. E. Winger, A. L. Rockwood, and R. D. Smith, "Internal Energy Effects on the Solvation and Reactivity of Multiply Charged Ions of Large Biomolecules for Electrospray Ionization Mass Spectrometry and Tandem Mass Spectrometry," presented at the 40th ASMS Conference on MS and Allied Topics, Washington, D.C., May 31-June 5, 1992.

Littlefield, R. J. "Communication Cost Models for Practical Applications." First Intel Delta Applications Workshop, Pasadena, California, February 11-12, 1992.

Loo, J. A., C. G. Edmonds, R. R. Ogorzalek-Loo, K. J. Light-Wahl, and R. D. Smith, "Electrospray Ionization and Tandem Mass Spectrometry of Noncovalent Protein Complexes," presented at the 40th ASMS Conference on MS and Allied Topics, Washington, D.C., May 31-June 5, 1992.

Loo, J. A., A. F. Fuciarelli, D. L. Springer, C. G. Edmonds, P. R. Ogorzalek-Loo, and R. D. Smith, "Elucidation of Covalent Modifications and Non-covalent Associations in Proteins by Electrospray Ionization Mass Spectrometry," presented at the 6th Symposium of the Protein Society, San Diego, California, July 25-29, 1992.

Loo, J. A., and R. D. Smith, "Tandem Mass Spectrometry of Large Multiply Charged Proteins with Electrospray Ionization," presented at the 40th ASMS Conference on MS and Allied Topics, Washington, D.C., May 31-June 5, 1992.

Mattiello, D. L., J. Callahan, T. Alam, J. Shiels, and G. P. Drobny, "Investigation of Broadband Quadrupolar Order for $I=1$ Spin Systems," presented at the 33rd Experimental Nuclear Magnetic Resonance Spectroscopy Conference, The Asilomar Conference Center, Pacific Grove, California, March 1992.

Mattiello, D. L., J. Callahan, T. M. Alam, G. P. Drobny, "Numerical Design and Analysis of Broadband Composite Pulses for $I=1$ Spine Systems," presented at ISMAR, Vancouver, B.C., 1992.

Mattiello, D. L., J. Callahan, T. Alam, J. Shiels, and G. P. Drobny, "Spin Alignment Studies of ^2H Labeled Nucleosides and Oligonucleotides," presented at the 36th Annual Biophysical Society Meeting, Houston, Texas, February 1992.

McCarthy, M. I., and A. C. Hess. "An Integrated Theoretical Approach for Studying the Interfacial Properties of Minerals." American Geophysical Union Spring Meeting, San Francisco, California, April 5-10, 1992.

- McCarthy, M. I., and A. C. Hess. "Theoretical Investigations of the Interfacial Properties of Environmentally Important Materials." 1992 American Geophysical Union Fall Meeting, San Francisco, California, December 7-11, 1992.
- McCarthy, M. I. "Theoretical Investigations of the Interfacial Properties of Environmentally Important Materials." Invited Lecture, University of Colorado, Boulder, Colorado, May 12, 1992.
- McDowell, R. S., "Basic Research in Molecular Sciences to Meet Environmental Needs," presented at the Portland State University Environmental Sciences and Resources Program, Portland, Oregon, May 21, 1992.
- McGill, R. A., and J. W. Grate, "Polymer/Surface Interfacial Effects on Surface Acoustic Wave Vapor Sensor Fabrication and Performance," presented at the 182nd Meeting of The Electrochemical Society, Toronto, Ontario, Canada, October 11-16, 1992.
- McRae, R. P., G. K. Schenter, and B. C. Garrett. "Solvent Effects on Activated Chemical Reactions: Zero-Point Energy Constraints and Quantum Mechanical Tunneling." West Coast Theoretical Chemistry Conference, Richland, Washington, May 21-23, 1992.
- Mohanty, S., and G. P. Drobney, " ^1H NMR Assignments of Holo-Neocarzinostatin in Solution," presented at the 33rd Annual ENC, The Asilomar Conference Center, Pacific Grove, California, 1992.
- Nicholas, J. B. "Periodic Hartree-Fock Investigations of a Zeolite Acid Site." 1992 American Geophysical Union Fall Meeting, San Francisco, California, December 7-11, 1992.
- Nicholas, J. B., J. C. White, and A. C. Hess. "A Comparison between the Ab Initio Electrostatic Surface of Zeolites and Partial-Charge Representations." 1992 West Coast Theoretical Chemistry Conference, Richland, Washington, May 21-23, 1992.
- Ogorzalek-Loo, R. R., J. A. Loo, H. R. Udseth, and R. D. Smith, "Applying Ion-Molecule Reactions to Studies of Gas Phase Protein Structure," presented at the 40th ASMS Conference on MS and Allied Topics, Washington, D.C., May 31-June 5, 1992.
- Ogorzalek-Loo, R. R., H. R. Udseth, J. A. Loo, and R. D. Smith, "Ion-Molecule Reactions of Proteins Studied with a Quadrupole Mass Spectrometer," presented at the 40th ASMS Conference on MS and Allied Topics, Washington, D.C., May 31-June 5, 1992.
- Ogorzalek-Loo, R. R., H. R. Udseth, and R. D. Smith, "Ion-Ion Reactions of Large Cations and Anions Generated by Electrospray Ionization," presented at the 40th ASMS Conference on MS and Allied Topics, Washington, D.C., May 31-June 5, 1992.
- Orlando, T. M., A. R. Burns, E. B. Stechel, and D. R. Jennison, "Quantum Resolved Studies of Radiation Induced Surface Reactions," presented at the Gordon Conference on Radiation Chemistry, Salve Regina College, Rhode Island, July 6-10, 1992.
- Orlando, T. M., "Electronically Stimulated Surface Reactions," presented at the Condensed Matter Seminar, Exxon Research and Engineering Company, June 23, 1992.
- Orlando, T. M., "Electronically Stimulated Surface Reactions," presented at the Physical Chemistry Seminar, Dept. of Chemistry, SUNY at Stony Brook, New York, June 25, 1992.
- Orlando, T. M., "Quantum Resolved Studies of Stimulated Surface Reactions," presented at the Physical Chemistry Seminar, Dept. of Chemistry, University of Washington, Seattle, April 29, 1992.
- Orlando, T. M., A. R. Burns, E. B. Stechel, and D. R. Jennison, "Quantum Resolved Stimulated Surface Reactions," presented at the International Workshop on Desorption Induced by Electronic Transitions (DIET V), Taos, New Mexico, April 1-4, 1992.
- Ornstein, R. L. "Coupling of Molecular Modeling and Experimental Studies for Rational Redesign of Substrate Specificity of Biodegradative Enzymes." 9th Annual Meeting of PANWAT, Richland, Washington, September 25, 1992.

Ornstein, R. L. "Molecular Dynamics Simulations of the Protein Ubiquitin: Comparison with X-Ray Crystal and Solution NMR Structures." Conference on Protein Receptors, University of Illinois, Urbana, Illinois, May 29-June 1, 1992.

Ornstein, R. L. "Rational Redesign of the Biodegradative Enzyme Cytochrome P450cam." SETAC '92, Richland, Washington, May 21-23, 1992.

Ornstein, R. L. "Rational Redesign of Biodegradative Enzymes for Environmental Cleanup." Invited Seminar at Washington State University-Tri-Cities, Richland, Washington, September 16, 1992.

Ornstein, R. L. "What Can You Learn from 'Long' Protein Molecular Dynamics Simulations: Ubiquitin?" University of Washington Department of Physics, Seattle, Washington, March 31, 1992.

Ornstein, R. L., M. D. Paulsen, and M. B. Bass. "Rational Redesign of the Biodegradative Enzyme Cytochrome P450 cam." 1992 West Coast Theoretical Chemistry Conference, Richland, Washington, May 21-23, 1992.

Paulsen, M. D., D. Filipovic, S. G. Sligar, and R. L. Ornstein. "Controlling the Regiospecificity and Coupling of Cytochrome P450cam." Sixth Symposium of the Protein Society, San Diego, California, July 25-29, 1992.

Peden, C.H.F., "Ceramic Catalyst Materials: Hydrous Metal Oxide Ion-Exchange Supports for Direct Coal Liquefaction," presented at the Sixth Annual Conference on Fossil Energy Materials, Oak Ridge, Tennessee, May 12-14, 1992.

Peden, C. H. F., "Preparation of Highly Dispersed Metal Catalysis Using Hydrous Titanium Oxide (HTO) Supports," presented at the 13th North American Meeting of the Catalysis Society, Pittsburgh, Pennsylvania, May 1992.

Peden, C.H.F., "The Interaction of Oxygen and Monolayer Metal Films on W(110)," presented at the 203rd National Meeting of the American Chemical Society, San Francisco, California, April 5-10, 1992.

Peden, C.H.F., "The Morphology of Oxide-Supported MoS₂," presented at the 7th Symposium of the Western States Catalysis Society, Albuquerque, New Mexico, March 19-20, 1992.

Peden, C.H.F., "The Morphology of Oxide-Supported MoS₂," presented at the Gordon Research Conference on Catalysis, New London, New Hampshire, June 29-July 3, 1992.

Peterson, K. A., and T. H. Dunning. "Applications of Correlation Consistent Basis Sets for First Row Atoms: CaS-Al Benchmarks." West Coast Theoretical Chemistry Conference, Richland, Washington, May 21-23, 1992.

Peterson, K. A., and H. J. Werner. "The Photodissociation and Photochemistry of ClO₂." West Coast Theoretical Chemistry Conference, Richland, Washington, May 21-23, 1992.

Poshusta, R. D., A. C. Hess, and M. I. McCarthy. "Ab Initio Studies of the Electronic Structure of Crystalline Nitric Acid Hydrates." 1992 West Coast Theoretical Chemistry Conference, Richland, Washington, May 21-23, 1992.

Poshusta, R. D., D. C. Tseng, A. C. Hess, and M. I. McCarthy. "Nitric Acid Monohydrate Crystal Calculations." Sanibel Symposia, St. Augustine, Florida, March 14, 1992.

Ray, D., "Reaction Dynamics in Size-Selected Molecular Clusters," presented at the Symposium on Structure and Dynamics of Large Molecular Clusters, 204th American Chemical Society National Meeting, Washington, D.C., August 23-28, 1992.

Ray, D., "Time Resolved Dynamics in Mass-Selected Clusters," presented at the SPIE OE/LASE, Los Angeles, California, January 23-25, 1992.

Ray, D., and K. W. Brown, "Structural Probes of Size-Selected Cluster Ions," presented at the 204th American Chemical Society National Meeting, Washington, D.C., August 23-28, 1992.

Ray, D., and R. D. Knochennuss, "Vibrations and Dynamics of Hydrogen-Bonded Clusters," presented at the 204th American Chemical Society National Meeting, Washington, D.C., August 23-28, 1992.

Rieke, P. C., D. R. Baer, G. E. Fryxell, M. H. Engelhard, and M. S. Porter, "Beam Damage of Self-Assembled Monolayers," presented at the Northwest Chapter of American Vacuum Society, Richland, Washington, September 1992; and American Vacuum Society National Symposium, Chicago, Illinois, November 1992.

Rockwood, A. L., and R. D. Smith, "How Do Electric Fields Effect Proton Transfer Reactions," presented at the 40th ASMS Conference on MS and Allied Topics, Washington, D.C., May 31-June 5, 1992.

Rose-Pehrsson, S. L., J. W. Grate, and M. Klusty, "A Surface Acoustic Wave Sensor Array System for Trace Organic Vapor Detection Using Pattern Recognition Analysis," presented at the The International Symposium on Environmental Sensing, June 22-26, 1992, Berlin, Germany. (Conference sponsored by the European Optical Society and the SPIE - International Society for Optical Engineering).

Sapers, S. P., "Photodissociation of $\text{BrCH}_2\text{CH}_2\text{OH}$ and $\text{ICH}_2\text{CH}_2\text{OH}$: OH ($X^2\Pi$) Product State Distributions by Laser-Induced Fluorescence," presented at the Western Spectroscopy Association, Asilomar Conference Center, Pacific Grove, California, January 1992.

Scamehorn, C. A., and M. I. McCarthy. "Interactions Between Water and the (001) Magnesium Oxide Surface as Described by Periodic Hartree-Fock Calculations." 1992 American Geophysical Union Fall Meeting, San Francisco, California, December 7-11, 1992.

Schenter, G. K., R. P. McRae, and B. C. Garrett. "Dynamic Solvent Effects on Activated Chemical Reactions: Effects of Reaction Path Curvature." American Chemical Society National Meeting, Washington, D.C., August 24-28, 1992.

Sherman, D. M. "Chemical Bonding and Electronic Transitions in the Earth's Deep Interior." Seminar at California Institute of Technology, Pasadena, California, March 9, 1992.

Sherman, D. M. "Electronic Structure and Chemical Reactivity of the Brucite $[\text{Mg}(\text{OH})_2]$ Surface." American Chemical Society National Conference, San Francisco, California, April 5-10, 1992.

Sherman, D. M. "Hydrogen Bonding and Proton Mobility in Minerals: Results from Periodic Hartree-Fock LCAO Calculations." American Geophysical Union Meeting, Montreal, Canada, May 12-15, 1992.

Sherman, D., M., and A. Skinner. "The High-Pressure Electronic Structure of FeO and the Significance of Spin-Pairing in the Earth's Interior." 1992 American Geophysical Union Fall Meeting, San Francisco, California, December 7-11, 1992.

Skinner, A. J., and J. P. LaFemina, "Atomic and Electronic Structure of the Calcite (10-14) Cleavage Surface," presented at the 13th Annual West Coast Theoretical Chemistry Conference, Richland, Washington, May 21-23, 1992.

Skinner, A. J., and J. P. LaFemina, "Atomic and Electronic Structure of the Calcite (10-14) Cleavage Surface," presented at the 203rd American Chemical Society National Meeting, San Francisco, California, April 5-10, 1992.

Skinner, A. J., and J. P. LaFemina, "Step Structure of the Calcite (10-14) Cleavage Surface," presented at the Environmental Interfaces Topical Conference, 39th Annual Symposium of the American Vacuum Society, Chicago, Illinois, November 9-13, 1992.

Skinner, A. J., J. P. LaFemina, and H. F. Jansen, "Total Energy Calculations of Calcite," presented at the 1992 Meeting of the American Physical Society, Indianapolis, Indiana, March 16-20, 1992.

Smith, R. D., D. R. Goodlett, J. H. Wahl, and H. R. Udseth, "High Performance Capillary Electrophoresis-Mass Spectrometry," presented at the 43rd Pittsburgh Conference & Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, Louisiana, March 9-13, 1992.

Smith, R. D., K. J. Light-Wahl, R. R. Ogorzalek-Loo, B. E. Winger, J. A. Loo, and A. L. Rockwood, "Experimental and Theoretical Methods for Probing the Higher Order Structure of Protein Ions in the Gas Phase," presented at the 40th ASMS Conference on MS and Allied Topics, Washington, D.C., May 31-June 5, 1992.

Smith, R. D., J. A. Loo, H. R. Udseth, A. L. Rockwood, B. E. Winger, R. R. Ogorzalek-Loo, and K. J. Light-Wahl, "New Methods and Instrumentation for the Characterization of Biopolymers Using Electrospray Ionization-Mass Spectrometry," presented at the BMS Kyoto '92, Osaka, Japan, September 20-24, 1992.

Smith, R. D., J. H. Wahl, D. R. Goodlett, H. R. Udseth, and C. J. Barinaga, "Capillary Electrophoresis-Mass Spectrometry in Peptide Mapping," presented at the ACS Annual Meeting, San Francisco, California, April 5-9, 1992.

Stahlberg, E. A. "Parallel Implementations of Full Configuration Interaction." Invited Lecture, Ohio State University, June 11, 1992, Columbus, Ohio.

Stave, M. W. "Full-Potential Linearized Augmented-Plane-Wave Calculations on Parallel Computers." West Coast Theoretical Chemistry Conference, May 21-23, 1992, Richland, Washington.

Thompson, M. A. "A Compound Essential to Life: A Theoretical Study of the Excited States of the Photosynthetic Reaction Center from *Rhodospseudomonas Viridis*." 47th Regional Meeting of the American Chemical Society, Missoula, Montana, June 18-19, 1992

Thompson M. A. "Biopolymer Molecular Dynamics on the Intel Delta." First Intel Delta Applications Workshop, Pasadena, California, February 11-12, 1992.

Tseng, T. C., R. D. Poshusta, A. C. Hess, and M. I. McCarthy. "Ab Initio Studies of the Electronic Structure of a Two-Dimensional Infinite Periodic Slab of Nitric Acid Monohydrate." West Coast Theoretical Chemistry Conference, Richland, Washington, May 21-23, 1992.

Trulson, M. O., D. M. Friedrich, and J. P. LaFemina, "Characterization of Photoinduced Charge Transfer Dynamics by Resonance Raman Spectroscopy," presented at the 1992 Spring Meeting of the American Chemical Society, Washington, D.C., August 1992.

Wahl, J. H., D. R. Goodlett, H. R. Udseth, and R. D. Smith, "Capillary Electrophoresis-Electrospray Ionizing Mass Spectrometry in Small Diameter Capillaries," presented at the 40th ASMS Conference on MS and Allied Topics, Washington, D.C., May 31-June 5, 1992.

Wahl, J. H., H. R. Udseth, and R. D. Smith, "Examination of Small-Diameter Coated Columns for High Sensitivity Capillary Electrophoresis-Mass Spectrometry of Proteins," presented at the 43rd Pittsburgh Conference & Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, Louisiana, March 9-13, 1992.

Wang, A. C., M. A. Kennedy, B. R. Reid, and G. P. Drobny, "RNA Purine Motion Studied by ^2H Solid State NMR," presented at the 33rd Annual ENC, The Asilomar Conference Center, Pacific Grove, California, April 1992.

Wang, A. C., M. A. Kennedy, B. R. Reid, and G. P. Drobny, "Solid-State NMR Investigation of Purine Motion in a 12 Base-Pair RNA Oligomer," presented at the 33rd Experimental Nuclear Magnetic Resonance Spectroscopy Conference, The Asilomar Conference Center, Pacific Grove, California, April 1992.

Wang, A. C., M. A. Kennedy, B. R. Reid, and G. P. Drobny, "Solid-State NMR Study of Purine Motion in a 12 Base-Pair Oligonucleotide," presented at the American Society for Biochemistry and Molecular Biology/Biophysical Society Joint Meeting, Houston, Texas, February 1992.

Wang, A. C., M. A. Kennedy, B. R. Reid, and G. P. Drobny, "Solution State and Solid State ^2H NMR Studies of Synthetic DNA and RNA Dodecamers: Relaxation and Dynamic Differences," presented at ISMAR, Vancouver, B.C., 1992.

White, J. C., and A. C. Hess. "Periodic Hartree-Fock Investigation of the Internal Surface of Siliceous Zeolites." 1992 American Geophysical Union Fall Meeting, San Francisco, California, December 7-11, 1992.

White, J. C., J. B. Nicholas, and A. C. Hess. "An *Ab Initio* Investigation of the Properties of Zeolites." 1992 West Coast Theoretical Chemistry Conference, Richland, Washington, May 21-23, 1992.

Winger, B. E., K. J. Light-Wahl, and R. D. Smith, "Ion-Molecule Reactions of Electrosprayed Ions Prior to Expansion into a Quadrupole Mass Spectrometer," presented at the 43rd Pittsburgh Conference & Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, Louisiana, March 9-13, 1992.

Winger, B. E., K. J. Light-Wahl, and R. D. Smith, "Probing Conformational Difference of Multiply Protonated Gas-Phase Ions Using Thermal Energy Hydrogen/Deuterium Exchange Reactions," presented at the 40th ASMS Conference on MS and Allied Topics, Washington, D.C., May 31-June 5, 1992.

Winger, B. E., J. A. Loo, H. R. Udseth, A. L. Rockwood, and R. D. Smith, "The Development of a Novel Electrospray Ionization-Fourier Transform Mass Spectrometer for the Investigation of Large Biomolecules," presented at the 40th ASMS Conference on MS and Allied Topics, Washington, D.C., May 31-June 5, 1992.

Wise, B. M., "Biased Regression for Dynamic Model Identification," presented to the University of Texas Department of Chemical Engineering, Austin, Texas, 1992.

Wise, B. M., "Monitoring the Health of Multi-Channel Analytical Instruments with Multivariate Statistical Process Control (MSPC)," presented at the Chemometrics in Analytical Chemistry '92, Montreal, Canada, 1992.

Wise, B. M., "The Effect of Biased Regression on Dynamic Model Identification," presented at the ANATECH '92, Lake Lanier Islands, Georgia, 1992.

Wise, B. M., "The Multivariate Statistical Process Control Approach to Process Diagnostics," presented at the ACS Symposium of Chemical Diagnostics for Chemical & Materials Synthesis Processes, San Francisco, California, 1992.

Wise, B. M., S. Lee, B. R. Holt, N. L. Ricker, and D. Haesloop, "A Comparison of Neural Networks and Nonlinear Biased Regression Techniques for Dynamic Model Identification," presented at the 1992 AIChE Annual Meeting, Miami Beach, Florida, 1992.

Wise, B. M., and D. J. Veltkamp, "Biased Regression for Identification of Dynamic and Statistical Process Control Models," presented at the Federation of Analytical Chemistry and Spectroscopy Societies XIX, Philadelphia, Pennsylvania, 1992.

Woon, D. E., and T. H. Dunning. "Correlation Consistent and Augmented Correlation Consistent Basis Sets for Second Row Elements Aluminum through Argon." West Coast Theoretical Chemistry Conference, Richland, Washington, May 21-23, 1992.

Xantheas, S. S., and T. H. Dunning. "Structures, Energetics, and Vibrational Frequencies of Negative-Ion/Water Clusters." West Coast Theoretical Chemistry Conference, Richland, Washington, May 21-23, 1993.

Xie, S. X., "Electron Transfer and Energy Transfer in Photosynthetic Systems," presented at the invited seminar at University of California, Santa Cruz, August 1992.

Xie, S. X., "Femtosecond Fluorescence Depolarization Study of Photosynthetic Antenna Proteins: Observation of Ultrafast Energy Transfer in Trimeric C-phyococyanin and Allophycocyanin," presented at the SPIE OE/LASE '92, Los Angeles, California, January 1992.

Appendix C

Activities

Appendix C

Activities

The following activities are described in this appendix: collaborations, colloquia speakers, technical advisory panel, and tours and visitors.

Collaborations

Topic: *Ab Initio* Calculations on Small Molecules by MØller-Plesset and Coupled Cluster Methods

Organization: Universität Bielefeld, Germany (H.-J. Werner)

MSRC Contact: K. A. Peterson

Topic: *Ab Initio* Density Functional Studies of the Structural and Electronic Properties of Carbonate Minerals

Organization: Oregon State University (J. Jansen) and Naval Research Laboratory (A. Skinner)

MSRC Contact: J. P. Lafemina

Topic: Acoustic Wave Sensors

Organization: University of California, Berkeley (R. White)

MSRC Contact: J. W. Grate

Topic: Adsorbate Dynamics in Molecular Inclusion Compounds

Organization: California Institute of Technology (M. E. Davis)

MSRC Contact: H. M. Cho

Topic: Adsorption in Polymers

Organization: University College, London (M. Abraham)

MSRC Contact: J. W. Grate

Topic: Advanced Graphical Programs

Organization: Eastern Washington University (R.W. Clark)

MSRC Contact: R. L. Ornstein

Topic: Advanced Mass Spectrometry

Organization: University of Washington, Seattle (T. N. Davis)

MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry

Organization: Washington State University, Pullman (J. D. Satterlee)

MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry

Organization: Washington State University, Pullman (R. Yount)

MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry

Organization: Washington State University, Pullman (C. R. Cremo)

MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry

Organization: Washington State University, Pullman (J.N.S. Evans)

MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry

Organization: Washington State University, Pullman (M. F. Smerdon)

MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry

Organization: University of the Pacific, San Francisco (M. F. Morales)

MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry

Organization: University of Illinois, Champaign-Urbana (S. G. Sligar)

MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry

Organization: Purdue University, West Lafayette (D. L. and J. D. Smith)

MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry
Organization: Children's Hospital Research
Institute (C.H.L. Schackleton)
MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry
Organization: North Carolina State University,
Raleigh (C. Hardin)
MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry
Organization: University of Delaware
(J. H. Futrell)
MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry
Organization: Cornell University, Ithaca
(F. W. McLafferty)
MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry
Organization: Hoffman-La Roche Inc.
(D. J. Liberato)
MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry
Organization: Lilly Research Laboratories
(R. N. Riggin)
MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry
Organization: Lederle Laboratories, American
Cyanamid Company
(M. M. Siegal)
MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry
Organization: ISIS Pharmaceutical
(R. Griffey)
MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry
Organization: Hybridon Inc.
(G. Fong)
MSRC Contact: R. D. Smith

Topic: Advanced Mass Spectrometry
Organization: Genentech
(W. Hancock)
MSRC Contact: R. D. Smith

Topic: Alkane Dehalogenase Structure-Function
Studies

Organization: University of Groningen,
The Netherlands
(D.B. Janssen, B. W. Dijkstra)

MSRC Contact: R. L. Ornstein

Topic: Application of Periodic Hartree-Fock Theory to
High-Pressure Geophysics

Organization: University of Torino, Torino, Italy
(R. Dovesi, M. Causa)

MSRC Contact: D. M. Sherman

Topic: Approximate Path-Integral-Based Methods
for Reactions in Solution

Organization: University of Pennsylvania
(G. A. Voth)

MSRC Contact: B. C. Garrett

Topic: A Priori Prediction of Optimal Models in
Continuum Regression

Organization: University of Washington
(B. Kowalski)

MSRC Contact: B. M. Wise

Topic: Atomic and Electronic Structure, and
Dynamics of Defects in Oxides

Organization: Materials Science Institute,
University of Oregon
(R. Haydock, A. Gibson)

MSRC Contact: J. P. LaFemina

Topic: Atomic and Electronic Structure, and
Dynamics of Surfaces

Organization: Xerox Webster Research Center
(C. B. Duke)

MSRC Contact: J. P. LaFemina

Topic: Atomic and Electronic Structure, and
Photophysical Properties of Polymers

Organization: Johns Hopkins University
(S. A. Kafafi)

MSRC Contact: J. P. LaFemina

Topic: Automobile Exhaust Catalysts

Organization: General Motors
(D. Belton)

MSRC Contact: C. H. F. Peden

Topic: Clay Mineralogy

Organization: University of Florida
(C. Johnston)

MSRC Contact: A. C. Hess

Topic: Comparison of Neural Networks, Genetic Algorithms and Non-Linear Biased Regression for Dynamic Model Identification

Organization: University of Washington
(B. Holt, L. Ricker)

MSRC Contact: B. M. Wise

Topic: Computer-Assisted Chemical Pattern Recognition

Organization: University of Pennsylvania
(P.C. Jurs)

MSRC Contact: R. L. Ornstein

Topic: Concurrent SuperComputer Consortium

Organization: California Institute of Technology
(P. Messina) and 12 other institutions

MSRC Contact: T. H. Dunning, Jr.

Topic: Continuum Power Regression in Configuration Space: An Improved Continuum Regression Method

Organization: University Laboratories, The Netherlands
(L. Ricker, S. deJong)

MSRC Contact: B. M. Wise

Topic: CPAC; Analytical Systems Development

Organization: University of Washington
(B. Kowalski)

MSRC Contact: B. M. Wise

Topic: Crystal Growth and Diffusion on Silicon Surfaces

Organization: University of Washington
(H. Jonsson)

MSRC Contact: L. R. Corrales

Topic: Cytochrome P450cam Structure-Function Studies

Organization: University of Illinois/Urbana
(S.G. Sligar), University of California/Irvine (T.L. Poulos)

MSRC Contact: R. L. Ornstein

Topic: Development of *Ab Initio*/Dynamics Methods for Studying the Chemistry and Physics at Mineral Interfaces

Organization: Daresbury Laboratory
(N. Harrison)

MSRC Contact: M. I. McCarthy

Topic: Development of Theoretical Methods for Studying Interfacial Dynamics

Organization: Hebrew University
(R. B. Gerber)

MSRC Contact: M. I. McCarthy

Topic: Development of Tight-Binding Electronic Structure Methods for Complex Oxides

Organization: Imperial College, London
(M. Foulkes)

MSRC Contact: J. P. LaFemina

Topic: Direct Participation of Solvent Molecules in Chemical Reactions

Organization: Sandia National Laboratory
(C. F. Melius)

MSRC Contact: B. C. Garrett

Topic: Discussion of Joint Research Program in the Use of "Rod Molecules" and Self-Assembled Monolayers to Synthesize, by Epitaxy, Difficult Materials, Such as Alumina Silicates

Organization: University of Colorado
(J. Michl)

MSRC Contact: S. Chambers

Topic: Effects of Fracture and Laser Pulses on Surface Damage and Particle Emission

Organization: University of Washington
(T. Dickinson)

MSRC Contact: D. R. Baer

Topic: Electronic Spectroscopy of Benzene-Water Clusters

Organization: Purdue University
(T. S. Zwier)

MSRC Contact: W. P. Hess

Topic: Electronic Structures of Transition Metal Oxides Using the FLAPW Method

Organization: Oregon State University
(H. Jansen)

MSRC Contact: D. M. Sherman

Topic: Electron Momentum Spectroscopy Studies

Organization: University of British Columbia
(C. E. Brion)

MSRC Contact: D. F. Feller

Topic: Electron/Water Chemistry

Organization: University of Sherbrooke
(L. Sanche)

MSRC Contact: T. M. Orlando

Topic: Excited-State Proton Transfer

Organization: University of California, Berkeley
(R. A. Mathies)

MSRC Contact: D. M. Friedrich

Topic: Experimental and *Ab-Initio* Studies of
2-Mercaptopyrimidine Tautomers

Organization: Aristotle University of Thessaloniki,
Greece (P. Akrivos)
University of Florida
(W. B. Person)

MSRC Contact: S. S. Xantheas

Topic: Experimental and Theoretical Investigations
of Hydrated Nitric Acid Crystals and Ice

Organization: University of Colorado
(S. M. George) and Washington
State University (R. D. Poshusta)

MSRC Contact: M. I. McCarthy

Topic: Experimental and Theoretical Investigations
of Environmentally Important Oxide Mineral
Surfaces

Organization: Texas A&M
(W. Goodman)

MSRC Contact: M. I. McCarthy

Topic: Experimental and Theoretical Studies of
Environmental Interfaces

Organization: University of Colorado
(S. George)

MSRC Contact: A. C. Hess, M. I. McCarthy

Topic: Fiber-Optic Laser Probes for Near-Field
Optical Microscopy

Organization: Digital Instruments Inc.
MSRC Contact: X. Xie

Topic: Force-Field Improvement for
Biomacromolecules

Organization: Roswell Park Cancer Institute and
S.U.N.Y. Buffalo (R. Rein)

MSRC Contact: R. L. Ornstein

Topic: Graphics Rendering Algorithms on Parallel
Processors

Organization: Washington State University
at Pullman
(C. Raghavendra, T-Y Lee)

MSRC Contact: J. B. Nicholas

Topic: High Performance Computational Chemistry

Organization: Argonne National Laboratory
(R. Stevens), Allied Signal, Amoco,
E. I. DuPont de Nemours and
Company, Exxon Research and
Engineering Company, and Phillips
Research Center

MSRC Contact: T. H. Dunning, Jr.

Topic: Hydrogen Bonding in Atmospheric Clusters

Organization: University of Washington
(R. O. Watts)

MSRC Contact: S. D. Colson, S. W. Sharpe

Topic: Hyperfine Properties of Small Radicals

Organization: Furman University
(L. B. Knight, Jr.)

MSRC Contact: D. F. Feller

Topic: Intramolecular Charge Transfer in Aromatic
Polyimides

Organization: Stanford University
(C. Rank, J. Salley)

MSRC Contact: J. P. LaFemina

Topic: Ion Solvation from Molecular Dynamics
Simulations

Organization: University of California,
San Francisco
(P. Kollman)

MSRC Contact: L. X. Dang

Topic: Ion Traps in Environmental Monitoring

Organization: Colorado School of Mines
(K. J. Voorhees)

MSRC Contact: S. L. Barlow

Topic: Light Source Base X-ray Diffraction Studies

Organization: University of Washington
(L. Sorenson)

MSRC Contact: D. R. Baer

Topic: Lignin Peroxidase Structure-Function Studies

Organization: Oregon Graduate Institute
(M. H. Gold), University of
California/Irvine (T.L. Poulos)

MSRC Contact: R. L. Ornstein

Topic: Low-Energy-Electron-Diffraction Study of
SnO₂ Surfaces

Organization: University of Texas at Austin
(J. Erskine, A. Kulkarni, D. Hinson)

MSRC Contact: J. P. LaFemina

Topic: Lubrication Chemistry

Organization: Battelle-Columbus
(B. Glaeser)

MSRC Contact: D. R. Baer

Topic: Massively Parallel Neural Net Approaches to
Protein Folding

Organization: Washington State University
at Pullman
(R. T. Miller, A. K. Dunker)

MSRC Contact: J. B. Nicholas

Topic: Measurement of SIFT Parameters

Organization: University of Colorado
(C. H. Depuy)

MSRC Contact: S. E. Barlow

Topic: Metal Oxide Interfaces

Organization: Sandia National Laboratory
(N. Shinn)

MSRC Contact: C. H. F. Peden

Topic: Methods for Treating the Electron Correlation
Problem

Organization: Harvey Mudd College
(R. J. Cave)

MSRC Contact: D. F. Feller

Topic: Microfabrication

Organization: University of Utah
(D. Petelenz)

MSRC Contact: J. Janara

Topic: Molecular Dynamics and *Ab-initio* Calcula-
tions on Chemical Reaction in Solution

Organization: IBM
(Jake Pacansky)

MSRC Contact: L. X. Dang

Topic: Molecular Dynamics Simulation of Gas
Diffusion in Silica Glasses

Organization: Oregon State University
(D. Way)

MSRC Contact: J. B. Nicholas

Topic: Molecular Dynamics Simulation of Xe
Diffusion in NaA Zeolite

Organization: University of Illinois at Chicago
(C. Jameson)

MSRC Contact: J. B. Nicholas

Topic: Molecular Models of Metal-Semiconductor
Heteroepitaxy

Organization: Montana State University
(J. Hermanson and A. Bowler)

MSRC Contact: J. P. LaFemina

Topic: Mustard Nerve Gas Biodegradation

Organization: Battelle Memorial Institute
(W. C. Tacon)

MSRC Contact: R. L. Ornstein

Topic: NMR Investigations of Defect Sites in Single
Crystal Minerals

Organization: California Institute of Technology
(G. R. Rossman)

MSRC Contact: H. M. Cho

Topic: NMR Studies of Nucleic Acid Chemistry

Organization: University of Washington
(G. P. Drobny, M. A. Kennedy,
B. R. Reid)

MSRC Contact: T. S. Tenforde

Topic: Organic Semiconductor Based Sensors

Organization: Bund University, Munich
(M. Liess)

MSRC Contact: M. Josowicz

Topic: Perturbed DNA Structure-Function-
Dynamics

Organization: Roswell Park Cancer Institute and
S.U.N.Y. Buffalo (R. Rein)

MSRC Contact: R. L. Ornstein

Topic: Phase Transitions and Critical Phenomena of Polymer Systems: Experiment and Theory

Organization: University of Maryland
(S. C. Greer)

MSRC Contact: L. R. Corrales

Topic: Photoelectron Spectroscopy of H-Bonded Clusters

Organization: University of Munich
(E. W. Schlag)

MSRC Contact: S. D. Colson

Topic: Polymer Coated Acoustic Wave Sensors

Organization: Sandia National Laboratory
(S. Martin)

MSRC Contact: J. W. Grate

Topic: Polymer Thin Films

Organization: Naval Research Laboratory
(R. A. McGill)

MSRC Contact: J. Janata

Topic: Quantal Calculations of Reaction Rates in Solution

Organization: Northwestern University
(G. C. Schatz)

MSRC Contact: B. C. Garrett

Topic: Reactions on High-Energy Surfaces: Destruction of Trichloroethylene

Organization: University of Pittsburgh
(J. T. Yates, T. H. Ballinger)

MSRC Contact: S. D. Colson

Topic: Real-Time Surface Reaction Dynamics

Organization: University of California, San Diego
(A. C. Kummel)

MSRC Contact: D. M. Friedrich, J. P. Cowin

Topic: Solid State Quantum Chemistry

Organization: University of Torino, Torino, Italy
(C. Pisani, R. Dovesi, C. Roetti)

MSRC Contact: A. C. Hess

Topic: Solid State Quantum Chemistry

Organization: Daresbury Laboratory, Daresbury, England
(V. R. Saunders, N. M. Harrison)

MSRC Contact: A. C. Hess

Topic: Structure Determination in Gallium Arsenide Single Crystals by NMR

Organization: California Institute of Technology
(D. P. Weitekamp)

MSRC Contact: H. M. Cho

Topic: Studies of Molecular and Spin Dynamics by Proton and Deuterium NMR

Organization: University of Washington, Seattle
(G. P. Drobny)

MSRC Contact: H. M. Cho

Topic: Support Quantum Mechanical Scattering Calculations to Determine the Crystal Structure and Lattice Parameters of the Metastable Phase from XPD Data

Organization: Montana State University
(R. Smith)

MSRC Contact: S. Chambers

Topic: Synthetic Radical Sites on Surfaces

Organization: University of Colorado
(G. B. Ellison)

MSRC Contact: J. P. Cowin, S. E. Barlow, T. M. Orlando

Topic: T4 Lysozyme Structure-Function Studies

Organization: University of Oregon
(B. W. Matthews, B. S. Hudson)

MSRC Contact: R. L. Ornstein

Topic: The Photochemistry of ClO_2

Organization: Universität Bielefeld, Germany
(H.-J. Werner); University of Colorado, Boulder (V. Vaida); University of California at San Diego (J. Simon)

MSRC Contact: K. A. Peterson

Topic: Theoretical Geochemistry

Organization: Arizona State University
(Paul F. McMillan)

MSRC Contact: A. C. Hess

Topic: Theoretical Geochemistry

Organization: University of Washington
(Subrata Ghose)

MSRC Contact: A. C. Hess

Topic: Theoretical Studies of Excited State Properties

Organization: University of Amsterdam
(G. de Brouckere)

MSRC Contact: D. F. Feller

Topic: Theoretical Studies of Excited State Potential Energy Surfaces

Organization: University of Idaho
(D. Edwards)

MSRC Contact: M. A. Thompson

Topic: Theoretical Studies of Heterogeneous Catalysis

Organization: Shell Development Corporation,
Houston, Texas
(T. Brownscombe, Mason Skiff)

MSRC Contact: A. C. Hess

Topic: Ubiquitin Dynamics

Organization: Eastern Washington University
(E. W. Small)

MSRC Contact: R. L. Ornstein

Topic: UV Resonance Raman Scattering from Charge-Transfer Complexes

Organization: University of Idaho
(J. L. McHale)

MSRC Contact: D. M. Friedrich

Topic: UV Resonance Raman Scattering from Intramolecular Charge-Transfer Compounds

Organization: University of Oregon
(B. S. Hudson)

MSRC Contact: D. M. Friedrich

Topic: Vacuum AFM and STM/AFM of Oxide Surfaces

Organization: University of Washington
(T. Engel)

MSRC Contact: D. R. Baer

Topic: Variational Transition State Theory

Organization: University of Minnesota
(D. G. Truhlar)

MSRC Contact: B. C. Garrett

Colloquia Speakers During 1992

Dr. Alain St. Amant, University of California

Dr. Kenneth Beck, University of Central Florida

Dr. David Bernholdt, University of Florida

Dr. Albert J. Bevelo, Iowa State University

Dr. Nina E. Bogdanchikova, Institute of Catalysis,
Russia

Dr. Bernard Brooks, National Institutes of Health

Dr. A. D. Buckingham, Cambridge University,
England

Dr. Alan Burns, Sandia National Laboratory

Dr. Michael A. Butler, Sandia National Laboratory

Dr. Karl F. Cantor, Bradeis University

Dr. Richard M. Caprioli, University of Texas

Dr. Robert J. Cave, Harvey Mudd College

Dr. Ai Chen, Syracuse University

Dr. Steven Chin, IBM Corporation

Professor Eric Chronister, University of California-
Riverside

Dr. Michael Connolly, New York University

Dr. Harry E. Cartland, Ballistic Research Laboratory

Dr. Zareh Darakjian, Ohio State University

Dr. Subhash Deshmukh, Tulane University

Dr. Eric Deumens, University of Florida

Dr. John Doyle, Massachusetts Institute of Technology

Dr. Dennis Duke, Florida State University

Dr. Mikhael N. Dulin, Institute of Thermophysics,
Russia

Dr. Robert C. Dunn, University of California-San Diego

Dr. Michael Dvorak, University of Minnesota

Dr. W. Matthew Foulkes, Imperial College, England

Dr. David Gale, Michigan State University

Professor Barbara J. Garrison, Pennsylvania State
University

Dr. Huodong Gat, University of Pennsylvania

Dr. Andrew J. Gratz, Livermore National Laboratory

Professor F. Peter Guengerich, Vanderbilt University
 Dr. Lawrence B. Harding, Argonne National Laboratory
 Dr. James Hart, Colorado State University
 Dr. William L. Hase, Wayne State University
 Dr. Dieter Hasselman, Ruhr University (Germany)
 Dr. Steven Heald, Brookhaven National Laboratory
 Dr. Michael Heath, University of Illinois
 Dr. Gina Hoatson, William and Mary College
 Dr. Chen Huang, University of California-Santa Barbara
 Dr. Bruce Hudson, University of Oregon
 Dr. John E. Jaffee, Michigan, Technological University
 Dr. Steve R. Jefferts, University of Colorado
 Dr. Jan Jensen, Iowa State University
 Dr. Mark Johnson, Yale University
 Dr. Hannes Johnsson, University of Washington
 Dr. Steven Just, Formal Systems, Inc.
 Dr. James F. Kelly, University of Idaho
 Dr. Peter A. Kollman, University of California-San Francisco
 Professor Andrew C. Kummel, University of California-San Diego
 Mr. Larry Lakin, Princeton University
 Professor Stephen R. Leone, Joint Institute for Laboratory Astrophysics/University of Colorado
 Dr. Pui-Tak Leung, Portland State University
 Dr. W. Carl Lineberger, Joint Institute for Laboratory Astrophysics
 Dr. Kevin Long, Baylor College of Medicine
 Dr. Gillian Lynch, University of Minnesota
 Dr. Gulzari L. Malli, Simon Fraser University, Canada
 Dr. Rudolph A. Marcus, California Institute of Technology
 Dr. Brian Matthews, University of Oregon
 Dr. William McCurdy, University of California

Professor James S. McElvain, Washington State University
 Dr. Andrew McIlroy, Sandia National Laboratory
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Acronyms and Abbreviations

Appendix D

Appendix D

Acronyms and Abbreviations

ABN	- aminobenzonitrile	CID	- collision-induced dissociation
ADC	- Analog-to-Digital Converter	cm	- centimeter
AES	- auger electron spectroscopy	COSY	- correlation spectroscopy
AFM	- atomic force microscopy	CPU	- central processing unit
AFS	- Andrew File System	CRADA	- Cooperative Research and Development Agreement
AMP	- adenosine 5'-monophosphate	CRPC	- Center for Research on Parallel Computation
amu	- atomic mass unit	CS&D	- Chemical Structure and Dynamics
ANL	- Argonne National Laboratory	CSCC	- Concurrent Supercomputer Consortium
ANN	- Artificial Neural Network	CSDRF	- Cluster Structure and Dynamics Research Facility
ANO	- atomic natural orbitals	CSF	- configuration state function
atm	- atmosphere	CT	- charge transfer (see Friedrich et al.)
AVS	- application visualization system	CVPP	- core-valence polarization potentials
BIN	- Backbone Information Network	CVT	- canonical variational theory
BLC	- bond-length conserving	CZE	- capillary zone electrophoresis
C2N	- computer-computer networks	DAP	- Data Acquisition Processor
CAD	- computer-aided design	DBMS	- database management systems
CAE	- computer-aided engineering	DCE	- Distributed Computing Environment
CAM	- computer-aided manufacturing	DCS	- Distributed Computing Systems
CASE	- computer-aided software engineering	DFS	- Distributed File Systems
CASSCF	- complete active space self consistent field	DMABN	- dimethylaminobenzonitrile
cc	- correlation consistent	DME	- distributed management environment
CCD	- charge-coupled-device	DNA	- deoxyribonucleic acid
CCIA	- Computational Chemistry Input Assistant	DNP	- dynamic nuclear polarization
CCSD	- coupled-cluster method	DOE	- U.S. Department of Energy
CDF	- common data format	DTEL	- Distributed Test and Evaluation Laboratory
CE	- capillary electrophoresis	EA	- electron affinity
CERN	- Center for European Nuclear Research	EASI	- electronic assistant for scientific investigation
CFS	- consolidated file system		
CI	- configurations interaction		

EBAL	- electron ballistic	GHz	- gigahertz
ECLS	- epitaxial continued layered structure	GLE	- generalized Langevin equation
EDS	- Environmental Dynamics and Simulation (program)	GUI	- graphical user interface
EFF	- empirical force field	GW	- gigawatt
EMSL	- Environmental and Molecular Sciences Laboratory	HF	- Hartree-Fock
EOCS	- epitaxial overlapping structure	HiPPI	- High-Performance Parallel Interconnect
EOTS	- epitaxial on top structure	Hz	- hertz
ER	- environmental restoration	I/O	- input/output
ESD	- electron stimulated desorption	ICCA	- integrated computational chemistry architecture
ESDIAD	- electron-stimulated desorption/ion angular distributions	ICR	- ion cluster resonance
ESI	- electrospray ionization	ICT	- intramolecular charge transfer
ESN	- End-user Subscriber Networks	ICVT	- improved canonical variational theory
ESR	- electron spin resonance	ID	- inside diameter
ESRC	- Environmental Sciences Research Center	IDL	- interface development laboratory
eV	- electron volts	IEEE	- Institute of Electrical and Electronics Engineers
EXAFS	- extended x-ray absorption fine-structure	IMPPT	- intramolecular Møller-Plesset perturbation theory
FaAA	- Failure Analysis Associates	INDO/S	- intermediate neglect of differential overlap spectroscopic
FCI	- full configuration interaction	IP	- ionization potential
FDDI	- Fiber Distributed Data Interface	IR	- Infrared
FID	- free induction decay	ISA	- Industry Standard Architecture
FIFO	- first in/first out	IS&S	- Information Systems and Services
FLAPW	- full-potential, linearized-augmented plane wave	IVR	- internal vibrational relaxation
fmol	- femtomole	JILA	- Joint Institute for Laboratory Astrophysics
fs	- femtosecond	JPL	- Jet Propulsion Laboratory (Caltech)
FT	- Fourier transform	kDa	- kilo-Dalton
FT-ICR MS	- Fourier transform ion cyclotron resonance mass spectrometer	kV	- kilovolt
FTICR	- Fourier transform ion cluster resonance	L	- liter
FTIR	- Fourier transform infrared	LANL	- Los Alamos National Laboratory
FY	- fiscal year	LAS	- laser ablation source
GA	- genetic algorithms	LCAO	- linear combination of atomic orbitals
Gbyte	- gigabyte	LDEI	- laser-driven electron impact
GC	- gas chromatography	LDF	- local density functional

LE	- locally excited (see Friedrich et al.)	NBO	- natural bond orbital (analysis)
LEED	- low-energy electron diffraction	NCAR	- National Center for Atmospheric Research
LEPD	- low-energy positron diffraction	NCSA	- National Center for Supercomputer Applications
LiF	- laser-induced fluorescence	NDDO	- neglect of diatomic differential overlap
LIMS	- laser ionization mass spectrometry	netCDF	- Network Common Data Format
LLNL	- Lawrence Livermore National Laboratory	NIH	- National Institutes of Health
LMMS	- Large Molecule Mass Spectrometry (program)	NIM	- network information management
<i>M</i>	- molar	NIST	- National Institute of Standards and Technology
MC	- Monte Carlo	NMR	- nuclear magnetic resonance
MCSCF	- multiconfiguration self-consistent field	NO	- nitric oxide
MD	- molecular dynamics	NOE	- nuclear Overhauser enhancement
MHz	- megahertz	NOESY	- nuclear Overhauser enhancement spectroscopy
MIMD	- multiple instruction-multiple data	NORCUS	- Northwest Colleges and Universities Association for Science
min	- minute	NP	- nonpolynomial
MIT	- Massachusetts Institute of Technology	NPT	- constant pressure and constant temperature
ML	- monolayer	ns	- nanosecond
mm	- millimeter	NSF	- National Science Foundation
MM	- molecular mechanics	NVE	- number of particles, volume, and energy
MNDO	- modified neglect of differential overlap	ODA	- oxydianiline
MP2	- second-order perturbation theory	ODBMS	- object database management systems
MP4	- fourth-order Moeller-Plesset	OEM	- U.S. DOE Office of Environmental Restoration and Waste Management
MPa	- megapascal	OER	- U.S. DOE Office of Energy Research
MPPT	- supermolecular Moeller-Plesset perturbation theory	OSF	- Open Software Foundation
MR-SDCI	- multireference singles and doubles configuration interaction	PAW	- Physics Analysis Workstation
MS	- mass spectrometry	PCA	- Principal Component Analysis
MSCF	- Molecular Science Computing Facility	pdvz	- polarized valence double zeta
MSRC	- Molecular Science Research Center	PEF	- potential energy function
MSS	- Molecular Science Software	PES	- potential energy surfaces
MW	- molecular weight	PET	- poly(ethylene terephthalate)
NAM	- nitric acid monohydrate	PMDA	- pyromellitic dianhydride
NASA	- National Aeronautics and Space Administration		
NAT	- nitric acid trihydrate		

PMF	- potential of mean force	SSD	- Scientific Supercomputing Division (Intel)
PNL	- Pacific Northwest Laboratory	STM	- scanning tunneling microscopy (microscope)
PP	- Pulse Programmer	TBTE	- tight-binding total energy
ppb	- parts per billion	TDMC	- time-dependent Monte Carlo
ps	- picosecond	TGL	- technical group leader
QMEFF-MD	- quantum mechanical empirical force field molecular dynamics	TICT	- twisted intramolecular charge transfer (twist-induced charge transfer)
QMMD	- quantum mechanical molecular dynamics	TIE	- total ion electropherogram
R2PI	- resonant two-photon ionization	TMS	- tandem mass spectrometer
RAID	- redundant arrays of inexpensive disks	TOF	- time-of-flight
REMPI	- resonance-enhanced, multiphoton-ionization	TRTA	- Time Resolved Transient Absorption
REP	- relativistic effective core potentials	TST	- transition state theory
RES	- reduced elution speed	TTOF	- Tandem Time-of-Flight
RF	- radio frequency	UC-B	- University of California-Berkeley
RFP	- request for proposals	UHF-NMR	- Ultrahigh frequency nuclear magnetic resonance
RGA	- residual gas analyzer	UHV	- ultrahigh vacuum
RHEED	- reflection high-energy electron diffraction	UI	- UNIX International
RISC	- reduced instruction set chip	UIMS	- User Interface Management Systems
RL	- U.S. Department of Energy Richland Operations Office	UV	- ultraviolet
RMS	- root mean square	V	- volt
RNA	- ribonucleic acid	VAF	- velocity autocorrelation functions
s	- second	VLSI	- very large scale integration
S	- Siemens	VME	- Versa Module Europa
SAC	- semiclassical adiabatic tunneling correction	VTST	- variational transition state theory
SAG	- semiclassical adiabatic ground-state	VUV	- vacuum ultraviolet
SC	- small-curvature	WM	- waste management
SCF	- self-consistent field	WSU	- Washington State University
SCSAG	- small curvature semiclassical adiabatic ground-state	WSU-TC	- Washington State University, Tri-Cities
SERC	- Science and Research Council	XAS	- x-ray adsorption spectroscopy
SNL	- Sandia National Laboratory	XDR	- external data representation
SPC	- simple point charge	XPS	- x-ray photoelectron spectroscopy
SPM	- scanning probe microscopy	ZEKE	- zero kinetic energy
		ZGF	- Zimmer Gunsul Frasca Associates

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