Molecular Science Research Center

Annual Report

January 1991

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

This document is printed on recycled paper.

Molecular Science Research Center

Annual Report

**M. L. Knotek
and the Staff of the MSRC**

January 1991

**Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
Richland, Washington 99352**

Contents

Opening Remarks

<i>M. L. Knotek</i>	v
---------------------------	---

Chemical Structure and Dynamics 1

1. A New Approach to Vibrational Spectroscopy of Clusters: The ZEKE Spectrum of the Phenol-Water Complex <i>S. D. Colson</i>	2
2. Surface Chemistry of Chlorinated and Fluorinated Hydrocarbons <i>J. P. Cowin, T. L. Gilton, M. R. Schneider, E. P. Marsh, and M. Kwini</i>	5
3. Spectroscopic Characterization of Species at and Above Oxidation Coupling Catalyst Surfaces <i>E. E. Gulcicek, R. S. Smith, and S. D. Colson</i>	7
4. Ultrahigh Vacuum Studies of Molecular Dynamics at the Water/Solid Interface <i>M. Kwini, T. L. Gilton, and J. P. Cowin</i>	8
5. High-Resolution Laser Spectroscopy of Small Molecules <i>R. J. Miller and S. D. Colson</i>	10
6. Ultrafast Time-Resolved Chemical Dynamics in Size-Selected Clusters <i>D. Ray</i>	14
7. High-Resolution Infrared Spectroscopy of Weakly Bonded Molecular Clusters <i>S. W. Sharpe</i>	15

Environmental Dynamics and Simulation 19

1. Quantum Chemistry of Clay Minerals <i>C. J. Hostetler and L. J. Criscenti</i>	19
2. Synchrotron Development <i>J. E. Amonette and S. V. Mattigod</i>	20

Macromolecular Structure and Dynamics 21

1. Preliminary Design of a Gigahertz NMR Spectrometer <i>T. S. Tenforde</i>	21
2. Large Molecule Mass Spectrometry <i>R. D. Smith, J. A. Loo, A. L. Rockwood, and H. R. Udseth</i>	24

Materials and Interfaces	31
1. Structure and Chemistry of Oxides and Mineral Surfaces <i>D. R. Baer, D. L. Blanchard, and M. H. Engelhard</i>	31
2. Multicomponent Solids NMR Development <i>B. R. Stults, J. A. Franz, J. C. Linehan, and J. Schaefer</i>	34
Theory, Modeling, and Simulation	37
1. Molecular Theory and Modeling <i>B. C. Garrett, G. K. Schenter, R. P. McRae, T. H. Dunning, Jr., and R. A. Kendall</i>	37
2. Materials Theory and Modeling <i>J. P. LaFemina, A. C. Hess, T. J. Godin, A. J. Skinner, G. K. Schenter, and D. L. Lessor</i>	44
3. Biomolecular Modeling and Simulation <i>R. L. Ornstein, M. D. Paulsen, M. B. Bass, G. E. Arnold, B. J. Lewis, G. A. Sanders, J. M. Smolen, S. L. van Wagoner, W. A. Jaquysh, and J. A. Braatz</i>	52
4. Molecular Science Software <i>R. A. Bair, D. F. Feller, R. A. Kendall, and T. H. Dunning, Jr.</i>	62
5. Workshops	70
Computing and Information Sciences	73
<i>E. W. Pearson</i>	73
Appendix A - MSRC Staff and Associates	A.1
MSRC Staff	A.1
MSRC Associates	A.16
Appendix B - FY 1990 Publications and Presentations	B.1
Publications	B.1
Manuscripts Not Yet Published	B.6
Presentations	B.9
Appendix C - Activities	C.1
Collaborations	C.1
Colloquia Speakers During FY 1990	C.3
Technical Advisory Panel	C.4
Tours and Visitors During FY 1990	C.5
Appendix D - Acronyms and Abbreviations	D.1

Computer and Information Sciences. Highlights on each of the program areas are given in the following paragraphs.

The Chemical Structure and Dynamics group is studying chemical kinetics and reaction dynamics of terrestrial and atmospheric processes as well as the chemistry of complex waste forms and waste storage media. Staff are using new laser systems and surface-mapping techniques in combination with molecular clusters that mimic adsorbate/surface interactions. They expect to generate new knowledge that will support geochemical modeling of contaminated soils, improve our understanding of the behavior of wastes in interim storage, lead to the development of novel approaches to remediation, and enable us to evaluate proposed treatment methods.

The Macromolecular Structure and Dynamics group is determining biomolecular structure/function relationships for processes that control the biological transformation of contaminants and the health effects of toxic substances. The group plans to develop a gigahertz NMR system that can be used in combination with advanced mass spectrometers to perform structural analyses of key enzymes and genetic material. This work will support the use of natural systems for bioremediation, guide the rational design of new systems having specific activity, and establish a molecular basis for health risk assessment.

The Materials and Interfaces program is generating information needed to design and synthesize advanced materials for the analysis and separation of mixed chemical waste, the long-term storage of concentrated hazardous materials, and the development of chemical sensors for environmental monitoring of various organic and inorganic species. Supporting facilities are being planned to synthesize novel materials; and instrumentation will be developed to study the structural, mechanical, electronic, and chemical properties of new materials.

The Theory, Modeling, and Simulation group is developing detailed molecular-level descriptions of the chemical, physical, and biological processes in natural and contaminated systems. Researchers are using the full spectrum of computational techniques. PNL's membership in the national consortium to acquire an Intel Touchstone Delta computer will give staff access to one of the world's most powerful computer systems. This capability will be used to model chemical and physical properties of wastes and contaminant interaction with soils and groundwater. The program will

produce knowledge needed to predict waste form behavior, suggest new remediation strategies, and support predictions of long-term consequences of proposed environmental restoration and waste management activities.

The Computer and Information Sciences group is developing new approaches to handle vast amounts of data and to perform calculations for complex natural systems. The EMSL will contain a high-performance computing facility, ancillary computing laboratories, and high-speed data acquisition systems for all major research instruments. The group is planning to develop an information system to speed communication of fundamental research results to application areas.

This year's report also includes a description of activities in Environmental Dynamics and Simulation. Although this work is being conducted by staff in the Environmental Science Research Center rather than the MSRC, it will eventually be housed in the EMSL and is closely related to the five MSRC research programs. The Environmental Dynamics and Simulation program is establishing a molecular-level understanding of the bonding forces and speciation of chemicals in colloidal suspensions and of chemicals sorbed on soils. A multidisciplinary approach will use controlled environmental chambers to simulate real-world conditions. Experimental results and theoretical analyses are expected to provide detailed descriptions of chemical reactions in complex mixtures and at solid/liquid interfaces. Resulting models will be used to predict the fate and transport of contaminant species and to provide a scientific basis for remediation schemes.

One of our primary goals, and a key action item identified by the DOE Review Committee, is to fill the remaining associate directorships in Macromolecular Structure and Dynamics, Materials and Interfaces, Computer and Information Sciences, and Environmental Dynamics and Simulation. Candidates have been identified for most of these positions, and several offers have been made. When these positions are filled, the programs can move ahead briskly.

As a result of an aggressive recruiting program in 1990, the MSRC staff now totals 50. This number includes 21 full-time scientists, 6 administrative personnel, 8 researchers assigned from other PNL organizations, 14 postdoctoral appointees, and 1 doctoral candidate. By the end of the next fiscal year, we expect our staff will have doubled. We plan to add 15 full-time scientists, 15 postdoctoral appointees,

Opening Remarks

This year—1990—was a year of accomplishment and progress for the Molecular Science Research Center (MSRC) and a year in which we achieved several major milestones for the Environmental and Molecular Sciences Laboratory (EMSL) construction project. As you will find in the sections that follow, our Chemical Structure and Dynamics program and our Theory, Modeling, and Simulation program are strongly developed and flourishing. Collaborations, memoranda of understanding, and other cooperative ventures have been established with nearly 30 universities, national laboratories, and industrial organizations. These agreements are extending the influence and impact of the MSRC and EMSL beyond the Pacific Northwest into all sections of the United States.

This fall, Energy Secretary James D. Watkins visited Richland to launch a new mission and vision for Hanford as the nation's preeminent environmental and ecological research and technology development center. Referring to Hanford as the "flagship" of DOE's environmental restoration and waste management program, Admiral Watkins called the EMSL "the teeth behind the rhetoric." He noted the need to find permanent solutions to long-term environmental problems, to improve our understanding of basic molecular chemistry, and to enhance our competitiveness in world markets for environmental services by capitalizing on the spin-off benefits. These goals are inherent in the EMSL mission to advance molecular science, apply new knowledge and technology to DOE needs, and involve the nation's scientific community in efforts to resolve environmental and waste management issues.

During the visit to Hanford, Secretary Watkins and Washington Governor Booth Gardner drafted a request for additional funding in FY 1991 for the new laboratory facility. Their efforts were successful. The Defense Appropriations bill passed by the 101st Congress earmarks \$20 million to accelerate development of the EMSL. As a result, the EMSL should be completed about 1 year earlier than originally planned. The facility is sponsored jointly by DOE's Office of Environmental Restoration and Waste Management and Office of Energy Research and is a line item in the FY 1991 DOE budget.

The first visit by the DOE Review Committee chaired by L. Edward Temple, Jr., was also a success. Re-

porting on the Technical, Cost, Schedule, and Management Review of the proposed EMSL conducted in May, the committee stated, "The intellectual challenge of the EMSL's mission is staggering. However, the practical payoff of success in this mission is immense, on the level of or perhaps beyond that of the Manhattan Project."

The Review Committee also commended our proposed research, noting that programs "... soundly connect fundamental research to practical DOE problems in the environmental area. . ." and stating that, "The forefront facilities at the EMSL, coupled with the integration of several scientific disciplines inside one laboratory, will ensure that the EMSL can contribute strongly to advanced education and training in the environmental area."

Such support is a welcome validation of Pacific Northwest Laboratory's (PNL's) firm commitment to the MSRC and EMSL. The years of discretionary internal investment are paying off, and we are encouraged to proceed even more aggressively with projects such as the development of the world's first gigahertz nuclear magnetic resonance (NMR) system and a cluster research facility.

Another completed 1990 milestone was the selection of the Zimmer Gunsul Frasca Partnership (ZGF) of Portland, Oregon, to provide architectural and engineering services. Our EMSL project team is looking forward to working with ZGF, which has received more than 80 national and local design awards since 1965. The firm's research laboratory projects include the Vollum Institute for Advanced Biomedical Research at the Oregon Health Sciences University; the Fred Hutchinson Cancer Research Center in Seattle, Washington; and the Earth and Marine Sciences building at the University of California-Santa Cruz.

Those of you who read our 1989 Annual Report will notice that we have done some fine-tuning and some program names have changed. Chemical Dynamics is now Chemical Structure and Dynamics. Chemistry and Interactions of Macromolecules has become Macromolecular Structure and Dynamics. Environmental Materials Chemistry was renamed Materials and Interfaces. And Information Architecture evolved into

5 technicians, 2 engineers, 3 associate directors, 2 project managers, 1 operations officer, and 7 administrative personnel.

These staff additions make space a major problem. To date, we have been occupying interim quarters within PNL's Physical Sciences Laboratory. During the coming year, we will expand our occupancy by establishing laboratories for the Materials and Interfaces program and the Macromolecular Structure and Dynamics program. Other PNL facilities will be used to house laboratories for the Computer and Information Sciences group and for cluster research.

During the past year, staff members contributed to or wrote more than 75 publications, and they have about 35 manuscripts awaiting publication. In addition, they made nearly 100 presentations at national and international events. The Colloquia Series, which began in 1989, also flourished. This year, 65 distinguished scientists visited PNL and the MSRC to share their knowledge and insight. They represented universities, research laboratories, and industry from across the United States as well as Canada, Israel, and Poland. In addition, we welcomed hundreds of visitors from academia, government, and industry.

Our outreach program also included workshops on *Planning for a Molecular Science Computer Center*; *High-Field Nuclear Magnetic Resonance*; *Application of*

Cluster Research to Environmental Problems; *Graphical User Interfaces in Computational Chemistry*; *Environmental Materials and Interfaces*; and *FTICR Design Criteria for Large Molecules*. During 1991, additional workshops will provide opportunities for prospective users to help us clarify the direction of MSRC research programs. Other input will be derived from the MSRC/EMSL User Committee being formed under the chairmanship of Professor Robert Watts, University of Washington.

We are pleased with our progress to date, but we recognize that many challenges and opportunities lie ahead. We are challenged by the Secretary of Energy's desire to accelerate completion of the EMSL; however, it is a most welcome challenge. We have an opportunity to create a scientific resource that will be unique within the United States and to lead efforts to find permanent solutions to environmental restoration and waste management problems. We have an opportunity to put teeth into DOE's goal to clean up its production sites and to develop the basic knowledge of chemistry that will enable us to provide solutions that are, in Secretary Watkins' words, "... better, safer, faster, and cheaper for the taxpayer."

Michael L. Knotek
Manager, Molecular Science Research Center

Chemical Structure and Dynamics

Chemical Structure and Dynamics

The scientific demands made by the environmental restoration and waste management effort are enormous. Advanced knowledge of interfacial chemistry is needed in order to develop methods for detecting, treating, and containing contaminants in the earth and its atmosphere. The required chemical understanding of the interfacial chemistry associated with pollution problems is essentially nonexistent, and an intensive program of fundamental research in this field is urgently needed.

The Chemical Structure and Dynamics program is developed around several initiatives in response to the need for a fundamental molecular-level understanding of chemistry at environmental interfaces. These initiatives are designed to develop the broad range of high-level capabilities required to mount a multilevel attack on the key scientific issues in this field. While the focus is on issues related to environmental materials chemistry, the impact is expected to extend into many fields essential to U.S. technological and economic strength.

The overall research philosophy is built around the established relationship between structure and function that is the underpinning of molecular science. The intent is to describe chemical processes at the molecular level in terms of the time evolution of the molecular structure under the control of potential energy functions.

The structural studies are key to the direct comparison with theory. Structures provide well-defined targets for testing theoretical assumptions. This is particularly important in dealing with the complex problems associated with the description of the molecule/substrate interface. Without good structural data, it will be very difficult to evaluate the quality of the potential functions generated by theory and needed to describe the molecular dynamics.

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. Chemical intuition based on homogeneous systems may be completely misleading. Second, they will provide the necessary data for the evaluation of molecular dynamics theories that are

being developed to describe molecular processes in terms of the kinematics of atomic nuclei on potential energy surfaces (PESs).

One 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. At the heart of this activity is a Cluster Structure and Dynamics Research Facility (CSDRF). The purpose of the CSDRF is to encourage cluster-based collaborative research on environmental chemistry using research tools of a scale and scope not readily available to individual researchers at university and industrial laboratories. A workshop attended by 50 scientists was held this year to discuss the development of the CSDRF. The workshop report discusses the relationship between cluster chemistry and pollution problems and outlines the basic requirements for developing the CSDRF as an effective collaborative user facility.

Another initiative brings a combination of state-of-the-art lasers and atomic resolution surface-mapping tools—scanning tunneling microscopy (STM) and atomic force microscopy (AFM)—to the study of interfacial chemistry and dynamics on extended structures. With the combination of lasers and surface-mapping tools, scientists can for the first time directly observe chemical process on realistic chemical surfaces rather than on idealized single crystal models. This initiative, in concert with the studies of molecular clusters, provides a new window through which we can observe untouched facets of condensed-phase chemistry and physics, expanding our understanding of the chemistry of materials science in ways that are expected to be far reaching.

The cluster and surface science initiatives illustrate two elements of a broad program including structure and dynamics studies of molecules in isolation, condensed in microstructures, in solution, and on extended surfaces. This multilevel, multidisciplinary approach allows for the dissection of complicated systems with the

anticipation that the study of the component parts will lead to a clearer understanding of complex chemical processes in nature.

1. A New Approach to Vibrational Spectroscopy of Clusters: The ZEKE Spectrum of the Phenol-Water Complex^(a)

S. D. Colson

The vibrational spectrum of the phenol-water cation complex is obtained by optical-optical double resonance threshold ionization spectroscopy with detection of the zero kinetic energy (ZEKE) electrons. The ZEKE signal only appears when the total photon energy is resonant with a level in the ion.¹⁻³ This work represents a new application of this method to molecular cluster vibrational spectroscopy. The results are a more accurate value of the ionization threshold and a well-resolved vibrational spectrum. Using this method, the precision of the vibrational frequencies is limited only by the laser resolution and/or the intrinsic properties of the molecular cluster (a few wavenumbers in this case). This result is in direct contrast to the usual photoelectron methods used to obtain vibrational spectra of ions where the width of the potential energy surface (PES) peaks (≥ 50 cm⁻¹) limits the resolution.

The one-to-one phenol-water complex is an ideal case for the development of the ZEKE method for obtaining vibrational spectra of cluster ions. The electronic spectrum of the intermediate (neutral) state shows large shifts with the addition of each water molecule^{4,5} (see Figure 1.1). Thus, by using threshold ionization spectroscopy, the spectra of the phenol-(H₂O)_n, $n=1-3$ complexes have been definitively identified and can be used as intermediate levels with little interference from other complexes.⁵ The $n=1$ complex shows activity from hydrogen-bonding vibrations that are also well resolved from absorptions by other complexes^{4,6} and can be used as intermediate levels to modify the vibrational activity in the ionization spectra.

The spectra shown in Figure 1.2 were obtained by a two-laser technique with detection of either ions

Figure 1.1. S_1 - S_0 absorption features for the phenol-(H₂O)_n complexes: Peak A is the phenol-H₂O origin band; Peak B, H₂O-wag; Peak C, the O-H...O-stretch; Peak D, the phenol-(H₂O)₂ origin region; and Peak E, the phenol-(H₂O)₃ origin band.

(Figure 1.2a) or ZEKE electrons (Figure 1.2b). This technique uses a pump laser to prepare an excited state of the complex and a probe laser for ionization of the excited species (Figure 1.3).

For Figure 1.2b, the pump laser was tuned to be resonant with the vibrationless origin (Peak A in Figure 1.1) of the lowest excited singlet state of the phenol-water complex (formed by the supersonic expansion of phenol and water in an argon carrier gas). The probe laser wavelength was then scanned through the threshold ionization region of the excited complex. ZEKE electrons are produced by ionization at threshold and at above threshold energies where the probe laser is resonant with rovibrational energy levels in the ion. In this way, the ionization energy and the rovibrational energies of the ion are revealed by the spectrum of the ZEKE intensity as a function of the probe laser energy. The energies of the peaks seen in Figure 1.2b are given in Table 1.1.

As shown in Figure 1.2a, the threshold ionization scan obtained by detecting the cluster ion yield⁵ rather than the ZEKE electron intensity consists of a series of steps due to increases in the ionization cross section as new ionization channels become available. Each step in the ion threshold scan corresponds to new resonances

(a) This work resulted from an Alexander von Humboldt Senior Science Award and was conducted at the Institut für Physikalische und Theoretische Chemie der Technischen Universität, Munich, Germany, in collaboration with G. Reiser, K. Müller-Dethlefs, and E. W. Schlag.

a) Detection of the cluster ion signal.

b) Detection of the ZEKE signal.

Figure 1.2. Pump-probe threshold ionization spectra of the phenol-water complex.

in the ZEKE spectrum. However, as is readily apparent, the increased resolution of the ZEKE method gives much more information concerning the nature of these resonances. The internal energies of the ion are more precisely defined and considerably more detail is revealed.

The ZEKE spectrum allows a more accurate determination of the adiabatic ionization potential (IP). After correcting for the effects of electric field in the ionization region, the ZEKE IP is $64,034 \pm 5 \text{ cm}^{-1}$ compared to $64,035 \pm 10 \text{ cm}^{-1}$, the value reported from ion threshold measurements.

Figure 1.3. Pump-probe threshold ionization spectra. The selected species are first excited to the desired vibronic intermediate state with the pump laser. The probe laser is then scanned through the energies required for formation of the ion at the ionization threshold or at higher thresholds reached by preparation of the ion in excited rovibronic states.

Table 1.1. Phenol-water ZEKE-detected cation vibrational spectrum.

Peak No.	Frequency Shift (cm^{-1})	Assignment ^(a) (ν_1, ν_2, ν_3)
0	(28025) ^(b)	(0,0,0)
1	239.9	(1,0,0)
2	255.9	(1,0,1)
3	449.1	(0,1,0)
4	476.9	(2,0,0)
5	493.2	(2,0,1)
6	518.8	phenol- ν_{6a}
7	680.3	(1,1,0)
8	713.4	(3,0,0)

(a) The ν_n mode numbering is simply taken in order of their appearance and has no other significance.

(b) S_1 -state ionization threshold.

The experimental effort and inherent uncertainties in the measurement of the IP are greatly reduced with ZEKE detection. First, with the ion threshold method, several careful measurements of the threshold curve at different extraction fields are needed to allow

extrapolation to the zero field value of the IP. Second, it is observed⁵ that the threshold becomes sharper at lower fields, a phenomena that may not be properly accounted for by the extrapolation. Finally, a somewhat arbitrary decision must be made about the location of the threshold for a step that is not infinitely sharp. For the ion threshold measurements,⁵ the threshold was assumed to be the maximum in a Gaussian function whose integrated form fit the observed threshold. This method selects the inflection point as the threshold, rather than the poorly defined onset. Considering all of these difficulties, the close agreement of the two values is quite rewarding.

Accurate values of the adiabatic IP will be very valuable in determining cluster binding energies. It is currently straightforward to obtain accurate cluster formation-induced shifts of transition energies and, now with ZEKE detection, IPs. Once the binding energy is known for either the ion or the ground or electronic excited state of the neutral cluster, this information can be combined with the observed shifts to obtain the binding energies in the other states. Binding energies, which are key to the evaluation of cluster binding theories, have proven to be one of the more difficult properties to measure.

The assignments in Table 1.1 show a harmonic progression in ν_1 that was assigned previously^{4,6} to be the hydrogen-bond stretching motion.^{5,6} There are two other hydrogen-bonding modes active in the spectrum. One shows up as two peaks (449.1 and 680.3 cm^{-1}) about 30 cm^{-1} to the red of the $2\nu_1$ and $3\nu_1$ bands. One possible assignment of the first of these peaks would be as a two- or threefold overtone of a lower frequency mode $n\nu_2$ in Fermi resonance with $2\nu_1$. The coupling term would need to be substantial in order to explain the intensity of $n\nu_2$. However, this makes it difficult to rationalize the harmonic $n\nu_1$ progression. The shifts due to Fermi resonance and anharmonicity would have to exactly cancel if there is to be no shift in the $2\nu_1$ frequency as would otherwise be expected for a strong Fermi resonance.

Also, it is unusual for the combination mode $n\nu_2 + \nu_1$ to be more intense than the fundamental $3\nu_1$ (the mode from which it "borrows" intensity in a Fermi resonance scheme) as is seen in Figure 1.2. An alternative would be to assign these two peaks as $\nu_1 + \nu_2$ and $2\nu_1 + \nu_2$. This, however, leaves the absence of activity of the ν_2 fundamental as an open question. The assignment suggested in Table 1.1 avoids the above concerns by assigning the peak at 449.1 cm^{-1} as

a new fundamental of that frequency that may or may not be *weakly* mixed with $2\nu_1$.

The low frequency of ν_3 and its coupling to ν_1 are particularly interesting. The lowest frequency mode in the neutral water dimer is predicted⁷ to have a value of about 100 cm^{-1} . The corresponding motion in the complex is a rotation of the phenyl ring around the hydrogen bond and would therefore be at a much lower frequency in the phenol-water cluster and may therefore be responsible for the 16- cm^{-1} mode in the phenol-water cation cluster. The intensity of ν_3 seems to be greater when ν_1 is also excited, suggesting that as the hydrogen bond is stretched the complex may twist, perhaps in response to steric forces that become more important as the hydrogen bond is weakened.

The definite assignment of ν_2 and ν_3 must be based on further experiments involving pumping of different intermediate levels (for example, the hydrogen-bonding "wag and stretch" motions that show up as Peaks B and C in Figure 1.1) and isotopic substitutions. The isotopic shifts will be quite sensitive to the nature of the vibrational motion, and the intensity factors for particular vibrations will depend strongly on the vibrational mode excited in the intermediate state.

These two approaches have proven to be very valuable in the analysis of the vibrational structure observed in the resonant-enhanced two-photon ionization PES spectrum of phenol, for example.⁸ It will be possible, for instance, to excite the hydrogen-bond bending or stretching motions in the S_1 state and observe the induced activity of the corresponding mode in the ZEKE spectrum.

The possibility for proton transfer in the cluster ion suggests the existence of at least two tautomers that may have similar energies. Crossing of the associated potential curves could cause unexpected effects in the observed vibronic intensities and frequencies that may not be amenable to explanation by the straightforward analysis proposed in Table 1.1.

The spectrum in Figure 1.2b also reveals one vibronic feature that is due to excitation of a phenol ring vibration. The strongest feature observed in our ZEKE spectrum of the bare phenol molecule is 516 cm^{-1} above the phenol IP. A peak at 516 cm^{-1} was also observed in the PES of phenol⁸ and assigned as ν_{6a} . Therefore, this mode is also assigned to the 518.8 cm^{-1} peak in the ZEKE spectrum of the complex, showing only a slight shift upon complexation.

This research will be continued in collaboration with E. W. Schlag and K. Müller-Dethlefs at Munich until the required equipment can be assembled at PNL. In addition to the study of clusters, the technique will be valuable in obtaining the rovibrational spectra of other species that are difficult to prepare except in molecular beams. Negative ion beams of low vapor pressure materials (metals, metal oxides, silicon oxide, etc.), radicals, and other reactive species can also be studied with the ZEKE technique.

References

1. M. Sander, L. A. Chewter, K. Müller-Dethlefs, and E. W. Schlag, *Phys. Rev. A* **36**, 4543 (1987).
2. W. Habenicht, R. Baumann, K. Müller-Dethlefs, and E. W. Schlag, *Ber. Bunsenges Phys. Chem.* **92**, 414 (1988).
3. G. Reiser, W. Habenicht, K. Müller-Dethlefs, and E. W. Schlag, *Chem. Phys. Lett.* **152**, 119 (1988).
4. A. Oikawa, H. Abe, N. Mikami, and M. Ito, *J. Phys. Chem.* **87**, 5083 (1983).
5. R. J. Lipert and S. D. Colson, *J. Chem. Phys.* **89**, 4579 (1988).
6. R. J. Lipert and S. D. Colson, *J. Phys. Chem.* **93**, 3801 (1989).
7. J. R. Reimers and R. O. Watts, *J. Chem. Phys.* **85**, 83 (1984).
8. S. L. Anderson, L. Goodman, K. Krogh-Jespersen, A. G. Ozkabak, R. N. Zare, and C. Zheng, *J. Chem. Phys.* **82**, 5329 (1985).

2. Surface Chemistry of Chlorinated and Fluorinated Hydrocarbons

J. P. Cowin, T. L. Gilton,^(a) M. R. Schneider,^(a)
E. P. Marsh,^(a) and M. Kwini^(a)

Surface reactions play a critical role in environmental problems in the soil and on atmospheric dust, sols, and

ices. The chlorinated and fluorinated hydrocarbons are especially important, as many of the former are persistent, prevalent groundwater contaminants, while both are important sources of stratospheric halogens that now threaten the ozone layer.

The cleavage of the halogen bond is crucial to the destruction of these molecules. These molecules can be cleaved by both electron rearrangement using ultraviolet photon adsorption or electron attachment in the gas phase. Recent studies for *adsorbed* molecules show how intertwined these two mechanisms can be. The following paragraphs discuss how electron transfers *between* the substrate and these adsorbed molecules can dramatically quench or promote halogen bond cleavage.

Our previous studies¹ showed that when a molecule is adsorbed directly on a metal surface its photochemical cross section is often sharply reduced compared to the same molecule in the gas phase or spaced one or more monolayers away from the surface. It was concluded that this reduction was due to a very fast competing charge transfer channel. The molecule CH_3Cl is photoexcited to a repulsive state by transferring a nonbonding halogen electron into the molecule's lowest empty orbital, an antibonding one. However, before the molecule can fragment (about 15 fs), this same electron can "hop" over to resonant, empty metal orbitals, as shown in Figure 2.1. The cation formed is not in a repulsive state; thus, the photofragmentation yield is reduced. The electron hopping time inferred from the large reduction in cross section is about 5 fs, which is in the middle of the range of recent theoretical results.^{2,3}

We designed an experiment to explore the above surmise and a converse reaction path. If a photon excites a substrate electron, as in Figure 2.1, this electron could lie resonant with the antibonding affinity orbital of the molecule. The anion formed should dissociate, as they do in dissociative electron attachment studies in the gas phase. The electron transfer mediated fragmentation should occur at wavelengths where the molecule shows no direct transitions. Thus, through wavelength studies, the electron transfer mediated fragmentation should be able to be isolated from the direct process. Also, the direct and indirect processes should produce completely different fragment kinetic energies.

Figure 2.2 shows the results for CH_3Cl adsorbed on a clean Ni(111) surface upon irradiation.^{4,5} The arrival times at the mass spectrometer of the ejected CH_3 radicals are shown.

(a) All then at the University of California-Santa Barbara.

Figure 2.1. Electron transfers quenching or promoting cleavage.

Figure 2.2. CH_3 radicals photoejected from CH_3Cl -covered nickel.

For 193-nm laser irradiation, two kinds of methyl radicals are produced. The fast 1.5-eV methyls come from the directly excited molecule, and the slower 0.7-eV methyls come from the dissociative electron

attachment process. At 248 nm, the molecule is not directly excitable; and correspondingly, only the 0.7-eV methyl peak is observed.

Note the results for irradiating increasing thicknesses of CH_3Cl . Only the topmost layer of CH_3Cl can contribute to the narrow time-of-flight (TOF) features. As expected, after 8 to 15 layers, the hot electrons can no longer reach the topmost layer, evidenced by the elimination of the slower of the two peaks. Both the direct and indirect channels are dramatically reduced in the first one to two monolayers from the surface due to quenching as the antibonding electron hops to the substrate very competitively with dissociation.

The above results^{4,5} gave for the first time a clear, conclusive demonstration of the role that electron transfer plays in laser surface chemistry, both in promotion and inhibition. Since many molecules containing O, halogens, S, P, or conjugated bonds show electron attachment induced dissociation or chemistry, this suggests that a broad class of useful surface processes may be accessible using laser stimulation. And very importantly, we have an excellent means of quantitatively probing the mechanisms.

We have further characterized the electron attachment induced surface photochemistry of CH_3Br , CCl_4 , CF_3Br , tetramethylsilane, and other molecules on $\text{Ni}(111)$ and CH_3Cl and CF_3Cl on $\text{GaAs}(100)$.

References

1. E. P. Marsh, M. R. Schneider, T. R. Gilton, F. L. Tabares, W. Meier, and J. P. Cowin, *Phys. Rev. Lett.* **60**, 2551 (1988).
2. P. Avouris and R. E. Walkup, *Ann. Rev. Phys. Chem.* **40**, 1 (1989).
3. P. Nordlander and J. C. Tully, *Phys. Rev. Lett.* **61**, 990 (1988).
4. E. P. Marsh, T. L. Gilton, W. Meier, M. A. Schneider, and J. P. Cowin, *Phys. Rev. Lett.* **61**, 2535 (1988).
5. E. P. Marsh, F. L. Tabares, M. R. Schneider, T. L. Gilton, W. Meier, and J. P. Cowin, *J. Chem. Phys.* **92**, 2004 (1990).

3. Spectroscopic Characterization of Species at and Above Oxidation Coupling Catalyst Surfaces

E. E. Gulcicek,^(a) R. S. Smith, and S. D. Colson

Methane is the world's most abundant hydrocarbon resource. Because most of this resource is being wasted instead of being used as a fuel or chemical source, a process known as oxidative coupling is being evaluated as a way to convert methane into more useful hydrocarbon molecules. This process is promising, but a more complete understanding of the reaction mechanism is needed to make the process more efficient. The formation of methyl radicals is believed to be an important intermediate reaction in the catalytic oxidative coupling of methane.

The first step in the proposed mechanism is the production of methyl from the reaction of methane with the catalytic surface. This step can be followed by the desorption of methyl into the gas phase, leading to the formation of higher molecular weight hydrocarbons via radical/radical combination and/or radical/substrate reactions.

In many previous experiments, the direct detection of the transient and unstable radical species was not possible. To determine the role of the methyl radical in the oxidative coupling process, direct measurements of the methyl radical and other reaction products were performed. This work relies on a new approach that quenches the reaction via a supersonic expansion into a vacuum followed by analysis using laser ionization mass spectrometry (LIMS).

Multiphoton ionization LIMS data, with the laser tuned to selectively ionize methyl, show a maximum in the gas phase methyl radical production rate as a function of temperature. The production of gas phase methyl nearly ceases at higher temperatures (about 800K).¹ Results obtained using vacuum ultraviolet (VUV) laser ionization (not yet published) and a recently developed laser-driven electron impact (LDEI) ionization² corroborate the multiphoton data. In addition, the VUV technique allows for the detection of several reaction products including C_2H_4 , C_2H_6 (indirectly), and C_3H_6 .

The C_2H_4 intensity versus temperature plot shows higher yields of C_2H_4 at temperatures beyond the

maximum for methyl radical production (Figure 3.1). The figure suggests that gas phase methyl radical species may not be directly involved in the oxidative coupling process.

This conjecture is further supported by the measured apparent activation energy for the formation of methyl radical since the relatively low value (30 Kcal/mole for the 1% Sr/La₂O₃ catalyst) is not consistent with the proposed gas phase radical coupling reaction mechanism. The formation of the methyl radical should be the energetic barrier for the process; but despite the low activation energy, high temperatures are required to drive the oxidative coupling process (Figure 3.1). Furthermore, the decrease in methyl radical production at higher temperatures is difficult to explain within the framework of a reaction mechanism based on gas phase methyl radicals.

An alternative explanation of the data is that a "change" in the catalyst occurs at some critical temperature. There are three possibilities: 1) a physical change such as a phase change or a change in the active site structure, 2) a chemical change in the

Figure 3.1. Oxidative coupling of methane over 1% Sr/La₂O₃ catalyst.

(a) Former NORCUS postdoctoral fellow.

structure of the catalyst, or 3) a chemical change in an absorbed surface species or the formation of new surface species.

This hypothesis leads to several important questions: What are the energy limiting reactions? Do these reactions occur in the gas phase or on the surface of the catalyst? What is the role of the catalyst? During the coming year, several experimental approaches will be used to answer these questions.

Temperature "jump" experiments are one method being used to determine a reaction mechanism. These experiments involve observing the effects of a perturbation (sudden temperature change) on the system. The premise is that physical changes (primarily due to temperature) will occur much faster than changes in chemical composition. These experiments can be used to determine what types of changes are occurring with the catalyst at various temperatures.

Isotopic studies will also be used to determine reaction pathways by providing clues about the source of various products. In one case, the oxygen in the feed gas is abruptly changed from $^{16}\text{O}_2$ to $^{18}\text{O}_2$ to determine whether oxygenated products arise from gas phase or surface reactions.

Reaction mechanisms will also be isolated by observing the isotopic distributions of the reaction products to reveal what species were involved and the type of collision process occurring in the reaction. In this experiment, reactions are performed with a 50/50 gas mixture of CH_4/CD_4 . Simple methyl radical recombination is not expected to result in isotopic scrambling, for instance, whereas other more complex mechanisms might.

References

1. E. E. Gulcicek, S. D. Colson, and L. Pfefferle, *J. Phys. Chem.* **94**, 7069 (1990).
2. E. E. Gulcicek, S. D. Colson, and L. Pfefferle, *Rev. Sci. Instrum.* (in press).

4. Ultrahigh Vacuum Studies of Molecular Dynamics at the Water/Solid Interface

M. Kwini,^(a) T. L. Gilton,^(b) and J. P. Cowin

Monolayer-by-monolayer deposition using molecular beams gives the opportunity to create highly structured layered surfaces. This is particularly true if done at sufficiently low temperature to prevent gross vertical diffusion.

Three areas are being studied using this controlled deposition. Work in two areas—complex single crystal mineral surfaces by epitaxy on conducting substrates and femtosecond dynamical studies on carefully spaced acceptor/donor pairs—is just beginning. Work in the third area—constructing water/solid interfaces of known structure—has already resulted in publications. Molecules and ions have been placed in and on top of these water layers, allowing direct measurement of electron transfer probabilities and femtosecond solvation dynamics.¹

Reactions at the water/solid interface are crucial to understanding both soil and atmospheric environmental reactions, many of which are photostimulated and/or involve an electron transfer. The water layer model systems provide a uniquely direct approach to these problems and to the general field of electrochemistry.

The molecule CH_3Cl was used as a "detector" of electrons. In a separate study,² 248-nm photons caused CH_3Cl to dissociate only through the photostimulated hot substrate electrons, causing dissociative electron attachment. By placing spacer layers of water between the surface and the CH_3Cl , the distances that the electrons are able to propagate through the water can be measured (see Figure 4.1).

(a) NORCUS graduate student from the University of California-Santa Barbara, funded by the National Science Foundation.

(b) Formerly at the University of California-Santa Barbara, now at Micron Technol.

Figure 4.1. Ultrahigh vacuum water/solid electron transfer model system.

At 50K, various thicknesses of water were deposited on a Ni(111) surface, upon which was next deposited typically one or four monolayers of CH_3Cl . The surface was then irradiated with a low-power 248-nm excimer laser. The ability of the photoexcited electrons with energies near the vacuum level to propagate through the water was measured by observing the yield of CH_3 in the normal direction or by measuring the cross section via the decrease in the surface CH_3Cl using thermal desorption spectrometry. Figure 4.2 shows the CH_3 photofragment yield at 248-nm versus water thickness. The distance behavior in Figure 4.2 measured by the loss of CH_3Cl roughly agrees with the fragment time-of-flight (TOF) yield.

The sharp increase for one monolayer of water placed on the surface occurs because the water prevents the electrons on the molecular anion from returning to the substrate on the time scale of the fragmentation. Without the water layer, the photoelectron chemistry is quenched. After peaking at two monolayers of water, the signal then decays roughly exponentially with the $1/e$ distance of about two monolayers. This decay indicates a very strong interaction of the electrons with the water spacer.

Figure 4.2. Electron transmission versus water depth.

It was not obvious whether the observed mean free path is due to elastic or inelastic encounters of the electron with the water. A very recent quantum calculation of electron motions in water multilayers resolves the issue: elastic scattering completely dominates.³ The strong electrostatic field around water is very effective at scattering 0 to 2-eV electrons. In contrast, similar experiments with xenon spacers showed a mean free path of well over 30 monolayers, consistent with what is known about electron mobility in liquid xenon.

Our measurement of the mean free path of low-energy electrons in water is not the first. However, it is unique in that it measures the transmission in the chemically important energy regime, with well-known structures, and it is extremely flexible.

As an example of its flexibility, rapid measurements were made of electron transmission for several spacer

molecules, detector combinations, and substrates. An experiment is in progress where ions are being added to the water multilayer, providing a well-known bias (measured by work function probes) and allowing the electrochemical Helmholtz layer to be built.

We also completed a related preliminary study of femtosecond solvation dynamics. The energy of the methyl fragment was about 0.6 eV, much faster than the 0.2 eV seen for gas phase dissociative electron attachment. This extra energy comes from that part of the solvation that can occur on the 20-fs time scale of the fragmentation. When a single monolayer of CH_3Cl was placed on hexane, CH_3Cl , or water, the energy of the ejected CH_3 ranged from 0.4 to 0.7 eV. Further studies and a theoretical collaboration will be conducted to uncover the mechanisms of this femtosecond solvation.

References

1. T. L. Gilton, C. Dehnhostel, M. R. Schneider, and J. P. Cowin, *J. Chem. Phys.* **91**, 1937 (1989).
2. E. P. Marsh, T. L. Gilton, W. Meier, M. A. Schneider, and J. P. Cowin, *Phys. Rev. Lett.* **61**, 2535 (1988).
3. R. N. Barnett, U. Landman, A. Nitzen, *J. Chem. Phys.* (in press).

5. High-Resolution Laser Spectroscopy of Small Molecules

R. J. Miller and S. D. Colson

Excited electronic states of a wide variety of diatomic and small polyatomic radicals are important components of flames, plasma discharges such as those used to prepare and process modern semiconductor materials, the atmospheres of the Earth and other planets, and regions of the interstellar medium. Many photodissociation reactions yield radical products in their ground or excited states. Here, "radical" is broadly defined to be any molecule having a ground electronic state possessing finite electron spin angular momentum. The presence of unpaired electrons endows these radicals with chemical and physical properties that differ substantially from those of closed-shell molecules.

The importance of these species is a reflection of their general lack of chemical stability: they are intermediates in many reactions. Additionally, the photo-physics of these species is of significance in the redistribution of incident radiant energy within planetary atmospheres and the interstellar medium. Fundamental studies of radicals will therefore contribute directly to a better understanding of the processes of photoionization, autoionization, and predissociation by which highly excited molecular states dispose of their energy.

Spectroscopic investigations yield information on energy level patterns, molecular parameters, and transition probabilities that characterize a molecule. Given appropriate knowledge, high-resolution spectroscopic studies can therefore identify radical species and monitor their abundances in remote or hostile environments. Photofragmentation processes can be more thoroughly understood by examining the quantum-state distributions of products that are revealed in such spectra. Accurate knowledge of the molecular parameters is useful in theoretical efforts ranging from comprehending the nature of molecules to modeling the behavior of complex dynamical systems. In the case of radicals, the fine structure and hyperfine structure interactions that are direct manifestations of the unpaired electron spin angular momentum are of particular interest.

An understanding of the structural and dynamical properties of a molecule requires an accuracy beyond the level of the Born-Oppenheimer approximation: the motions of the nuclei and the electrons cannot be treated independently. Terms neglected in the Born-Oppenheimer approximation include couplings between zero-order wave functions associated with the different electronic states of the molecule. These interactions, known as perturbations, can strongly influence many molecular properties, including energy-level patterns, spontaneous and stimulated transition probabilities, radiative lifetimes, as well as autoionization, predissociation, and isotope-selective photodissociation phenomena.

Fine structure interactions are often dominated by perturbations involving the electron spin, the electron orbital, and the nuclear rotational angular momenta. Experimental determination of the dependence of fine structure parameters on vibrational and rotational excitation thus provides a sensitive probe of perturbation mechanisms and of the structural and dynamical ramifications of these perturbations.

Couplings involving the nuclear spin angular momentum are known as hyperfine interactions. The parameters used to characterize the magnetic hyperfine interactions yield detailed structural information that is specific to the orbital and spin distributions of the unpaired electrons. In excited states, as in the ground states of radicals, these unpaired electrons typically occupy the outermost orbitals that are so important in defining the chemical and physical properties of a molecule.

Fine structure and hyperfine structure interactions can profoundly influence dynamical phenomena. An excellent example are the theories currently being developed to treat the dynamics of photoinduced ionization that are revealed in photoelectron angular distributions measurements.¹⁻⁵ Analyses of such distributions require accurate and precise fine structure and hyperfine structure parameters to account for bound-state phenomena such as loss of coherence¹⁻³ and loss of optical alignment⁵ that affect the observed anisotropies of the angular distributions. Such experimental values also provide objective criteria for evaluating trial molecular wave functions.

Current research activities focus on fundamental spectroscopic investigations of the molecule nitric oxide (NO). The practical interest in this radical follows largely from its role in the chemistry and physics of the upper atmosphere: NO is directly involved in the ozone cycle, and it is a major industrial pollutant.

There is a long-standing interest in the $A^2\Sigma^+$, $D^2\Sigma^+$, and $C^2\Pi$ Rydberg states and the $B^2\Pi$ and $a^4\Pi$ valence states of NO that lie in the region of the ground-state dissociation limit. Historically, research has focused on understanding the dynamics of the processes of molecular predissociation and inverse predissociation of N and O atoms that occur in the mesosphere and stratosphere.

The higher excited states of NO are also of considerable interest. The electronic configuration of NO, with its closed-shell $1\Sigma^+$ ionic core, yields a series of Rydberg and valence states that have remarkably different properties. Experimental and theoretical investigations of these states have already revealed a wealth of interstate couplings and have contributed greatly to a growing understanding of such perturbations. Additionally, this molecule can be treated at a theoretical level sufficient to afford an excellent opportunity for quantitative interpretation of these interactions.

Initial studies demonstrated the utility of ultrahigh-resolution continuous-wave laser sources in multiphoton spectroscopy. Doppler-free fluorescence excitation spectra resulting from two-photon pumping of $(3s\sigma)A^2\Sigma^+(v'=1, N'=3) \leftarrow X^2\Pi(v''=0)$ $^{14}\text{N}^{16}\text{O}$ have been measured that amply reveal the fine structure and hyperfine structure splittings within selected rovibronic levels of $A(v=1)$, and the parameters characterizing these spin interactions have been extracted from the experimental observations.⁶

The $A \leftarrow X(1,0)$ band has now been examined in greater detail. The frequencies of 351 two-photon rotational transitions have been measured with Doppler-free resolution. Analyses of these data yielded improved values for the phenomenological rotational and centrifugal distortion constants B_v and D_v and the first systematic determinations of the third-order rotational constant H_v and of the fine structure parameter γ_v describing the $(3s\sigma)A^2\Sigma^+(v=1)$ Rydberg state of $^{14}\text{N}^{16}\text{O}$. A paper describing these results is being prepared.

The effective cross section for two-photon excitation of $R_{11}(J''=2.5)$ has been estimated to be $1 \times 10^{-44} \text{ cm}^4 \cdot \text{s}$.⁶ The large magnitude of this cross section makes NO an unusually favorable candidate for investigations using the low intensities available with continuous-wave dye lasers. However, the general applicability of ultrahigh-resolution studies to molecules will require development of new pulsed laser sources that retain the necessary spectral resolution while delivering higher field intensities. Efforts are in progress to develop such sources utilizing pulse amplification of ultrahigh-resolution continuous-wave dye laser fields with a long-pulse (250-ns) excimer laser.

The $(4p\pi)K^2\Pi(v=2)$ and $(3d\delta)F^2\Delta(v=3)$ Rydberg states of $^{14}\text{N}^{16}\text{O}$ have been studied using $(2+1')$ optical-optical double resonance laser-induced fluorescence (LIF) dip techniques.⁷ These experiments employed two ultrahigh-resolution continuous-wave dye lasers. The term energies and lifetimes of 60 individual rovibronic levels of the $(4p\pi)K^2\Pi(v=2)$ state and 11 individual rovibronic levels of the $(3d\delta)F^2\Delta(v=3)$ state (results not yet published) were measured. The full rotational envelope of the $F \leftarrow X(3,0)$ band was examined further in $(1+1')$ multiphoton ionization experiments using high-resolution, tunable, vacuum ultraviolet light (a paper is being prepared describing these results).

The observed term energies (Figure 5.1) yield evidence for the occurrence of spin-uncoupling phenomena within the $K(v=2)$ levels; and weak mutual perturbations were observed for both e and f symmetry components of $K(v=2)$ and $F(v=3)$ rotational levels in the region of $N = 10$ to 13. The observed lifetimes (Figure 5.2) dramatically confirm the existence of these mutual perturbations and exhibit quite complex dependencies on the total angular momentum. The magnitudes of the $K(v=2)$ lifetimes are generally consistent with expectations based on postulated, competing homogeneous and heterogeneous predissociation channels involving the $a^4\Pi$ continuum and the $(4p\sigma)M^2\Sigma^+$ Rydberg state, respectively.⁹ A more complete understanding of the structural and dynamical properties of these states will require a detailed theoretical analysis of the complex multistate perturbations occurring in this energy region.

Figure 5.1. Reduced term energies of e and f symmetry levels of the $K^2\Pi(v=2)$ and $F^2\Delta(v=3)$ states as a function of N . The quantum number N , where $N = J-S$, is appropriate for Hund's case (b) coupling consistent with observations at high J values. Energy shifts resulting from the weak $K^2\Pi(v=2) \sim F^2\Delta(v=3)$ perturbation are readily discerned in the region of the curve crossings near $N = 10$ to 13.

Figure 5.2. Lifetimes of the F_2^e and F_2^f levels of $K^2\Pi(v=2)$ and the F_2^f levels of $F^2\Delta(v=3)$ as a function of N . The $F(v=3)$ lifetimes have been divided by 10 for clarity. The lifetimes of the f symmetry levels readily manifest the effects of the weak $K^2\Pi(v=2) \sim F^2\Delta(v=3)$ perturbation in the region of $N = 10$ to 13. The radiative lifetime of unperturbed levels of $F(v=3)$ is 28.6 ± 1.4 ns.⁸ The F_1 spin components exhibit qualitatively similar behavior.

In many experiments—including those designed to scrutinize spin-rotation and hyperfine interactions,¹⁰⁻¹¹ structural and dynamical ramifications of weak perturbations,¹² and photoelectron angular distributions¹⁻⁵—it is desirable to excite selectively to a *single, completely specified* quantum level (for example, one hyperfine level) within the resonant intermediate state. Under such conditions, observed splittings directly characterize couplings within the upper electronic state of interest. Furthermore, interpretation of dynamical information is freed from complications arising from, for example, initial preparation of some coherent superposition of hyperfine structure or fine structure levels.

The spectral resolution currently available from pulsed lasers will in general preclude attainment of this

objective. Ultimately, in conjunction with molecular beam techniques, ultrahigh-resolution excitation sources will yield the desired objective of *single* quantum-state selectivity.

This research program is a collaborative effort involving Professor Vincent McKoy, Department of Chemistry, California Institute of Technology; Dr. Robert N. Compton, Health and Safety Research Division, Oak Ridge National Laboratory; and Bruce A. Bushaw and Dr. Wallace L. Glab, Materials and Chemical Sciences Center, PNL. This approach combines the theoretical expertise of the Cal Tech group, the vast experience of the Oak Ridge group in the field of photoelectron spectroscopy, and the ultrahigh-resolution spectroscopic capabilities available at PNL.

This program will yield experimental results previously unavailable to investigations of the excited electronic states of small molecules. The resulting new information will substantially enhance our understanding of the processes that are initiated by interactions of matter with high-energy photons and ionizing radiation. The full scientific ramifications of these results will be ensured by the close interactions of the experimental and theoretical research teams. This research is predominantly supported through DOE's Office of Health and Environmental Research.

References

1. R. N. Compton, J.A.D. Stockdale, C. D. Cooper, X. Tang, and P. Lambropoulos, "Photoelectron Angular Distributions from Multiphoton Ionization of Cesium Atoms," *Phys. Rev. A* **30**, 1766 (1984).
2. W. Christian, R. N. Compton, J.A.D. Stockdale, J. C. Miller, C. D. Cooper, X. Tang, and P. Lambropoulos, "Near-Infrared Multiphoton Ionization of Cesium," *Phys. Rev. A* **30**, 1775 (1984).
3. A. Dodhy, J.A.D. Stockdale, R. N. Compton, X. Tang, P. Lambropoulos, and A. Lyras, "Two-Photon Resonant Three-Photon Ionization of the $nd\ ^2D$ States of Cesium, Rubidium, and Sodium: Photoelectron Angular Distributions," *Phys. Rev. A* **35**, 2878 (1987).
4. R. L. Dubs, S. N. Dixit, and V. McKoy, "Circular Dichroism in Photoelectron Angular Distributions as a Probe of Atomic and Molecular Alignment," *J. Chem. Phys.* **85**, 656 (1986).
5. J. R. Appling, M. G. White, R. L. Dubs, S. N. Dixit, and V. McKoy, "Circular Dichroism in Photoelectron Angular Distributions from Two-Color (1+1) REMPI of NO," *J. Chem. Phys.* **87**, 6927 (1987).
6. R. J. Miller, W. L. Glab, and B. A. Bushaw, "Two-Photon Spectroscopy at Ultrahigh Resolution: Fine Structure and Hyperfine Structure of the $(3\sigma)4\ ^2\Sigma^+(v=1, N=3)$ Rydberg State of NO," *J. Chem. Phys.* **91**, 3277 (1989).
7. R. J. Miller and B. A. Bushaw, "Continuous Wave-Continuous Wave Molecular Double Resonance Spectroscopy: Lifetimes and Term Energies of Individual Rovibronic Levels of the $(4p\pi)K\ ^2\Pi(v=2)$ Rydberg State of Nitric Oxide," *J. Chem. Phys.* **92**, 3245-7 (1990).
8. D. J. Hart and J. W. Hepburn, "Vacuum Ultraviolet Laser Spectroscopy: Radiative Lifetimes of Interacting $^2\Delta$ States of NO," *J. Chem. Phys.* **86**, 1733 (1987).
9. R. J. Miller, L. Li, Y. Wang, W. A. Chupka, and S. D. Colson, "Multiphoton Ionization Studies of NO: Spontaneous Decay Channels in the $(4p\pi)K\ ^2\Pi(v=2)$ Rydberg State," *J. Chem. Phys.* **90**, 754-61 (1989).
10. G. Meijer, M. Ebben, and J. J. ter Meulen, "High-Resolution Study of the $NO\ E\ ^2\Sigma^+ \leftarrow A\ ^2\Sigma^+$ Transition by Pulsed-cw Double Resonance," *Chem. Phys. Lett.* **147**, 525 (1988).
11. G. Meijer, M. Ebben, and J. J. ter Meulen, "High-Resolution Spectroscopy of Highly Excited Electronic States by Pulsed-cw Double Resonance in a Molecular Beam. A Study of the $NO(E-A)$ System," *J. Chem. Phys.* **127**, 173 (1988).
12. E. E. Eyler, W. A. Chupka, S. D. Colson, and D. T. Biernacki, "Autoionization of the $4f$ Rydberg State of the NO Molecule," *Chem. Phys. Lett.* **119**, 177 (1985).

6. Ultrafast Time-Resolved Chemical Dynamics in Size-Selected Clusters

D. Ray

Small molecular complexes have been used to prepare reactants in well-defined orientations to elucidate the dynamics of simple chemical reactions.^{1,2} Similarly, larger clusters have been used to examine the effects of solvation on the energetics of chemical reactions.^{3,4}

Recent experiments exploring the effects of solvation on the *dynamics* of chemical reactions⁵⁻⁷ indicate the feasibility of real-time measurements of intracluster dynamics and furthermore suggest that such measurements may provide qualitatively new information on chemical dynamics in a microsolvent environment.

The real-time measurements were obtained by combining techniques of time-of-flight mass spectrometry (TOF-MS) and picosecond time-resolved pump-probe spectroscopy. The clusters were generated in pulsed gas expansions. In the work of Ray et al.⁵ on the photodissociation and recombination dynamics of I_2 in size-selected $I_2(CO_2)_n$ clusters, cluster size selection was effected by TOF-MS prior to interaction with the picosecond laser pulses. A subsequent reflectron-type TOF-MS was used to mass analyze the ionic photoproducts. Measurement of the photoproducts as a function of the time delay between the initial "pump" pulse (which dissociates I_2) and the subsequent "probe" pulse (which monitors the reappearance of ground state I_2) provided information on the dynamics of recombination and vibrational relaxation.

The results, shown in Figure 6.1, show two interesting features. First, the dynamics show a marked dependence on cluster size. Second, the process (recombination plus vibrational relaxation) is significantly faster than the analogous process measured for neutral I_2 in molecular liquids, where recombination plus vibrational relaxation takes 50 to 150 ps.⁸ The cluster results are currently not well understood.

The time-resolved measurements of chemical dynamics involving intermolecular proton transfer reactions from an optically excited "donor" molecule to the surrounding solvent were performed on mass selected neutral clusters.^{6,7} In these experiments, in contrast to the recombination dynamics discussed above, the dynamics do not appear to have a strong dependence on cluster size. Steadman and Syage were able to fit their data on phenol(NH_3)_n clusters⁷ to a phenomenological model

Figure 6.1. Absorption recovery data for $I_2(CO_2)_{16}$ (open circles) and $I_2(CO_2)_9$ (filled circles) as a function of time delay between 720-nm pump and probe pulses. Since the pump and probe pulses are equivalent, the data are symmetric about 0-ps delay. The asymptotic values have been scaled to the quantum yield for recombination as determined in a separate experiment. Also shown are single exponential recoveries: 30 ps for $I_2(CO_2)_9$ (dashed line) and 10 ps for $I_2(CO_2)_{16}$ (solid line), convoluted with the instrument response function (Gaussian, $\sigma=3$ ps, due to counterpropagating pump and probe pulses).

used for excited-state proton transfer in liquids.⁹ There is no molecular-level theory for proton transfer in condensed phase; indeed, the reaction coordinate for proton transfer is unknown. Existing mass spectrometric capabilities in the MSRC are being augmented to facilitate the study of ultrafast chemical dynamics in neutral clusters using techniques of ultrafast laser spectroscopy designed to monitor the flow of vibrational energy in intracluster chemical dynamics.

A tandem TOF-MS is currently being developed in the MSRC for real-time studies of chemical dynamics in cluster ions. This instrument will allow a wide variety of action spectroscopies (for example, photoproduct analysis; ultrafast time-resolved absorption, emission, and photoelectron spectroscopies) to be performed on large (<100 constituents) mass selected clusters. These clusters correspond to a molecule or reactive system surrounded by up to two solvation shells, an important size range for condensed-phase dynamics.

References

1. C. Wittig, S. W. Sharpe, and R. A. Beaudet, *Acc. Chem. Res.* **21**, 341 (1988).
2. N. F. Scherer, L. R. Khundkar, R. B. Bernstein, and A. H. Zewail, *J. Chem. Phys.* **87**, 1451 (1987).
3. R. Knochenmuss and S. Leutwyler, *J. Chem. Phys.* **91**, 1268 (1989).
4. J. F. Garvey and R. B. Bernstein, *Chem. Phys. Lett.* **143**, 13 (1988).
5. D. Ray, N. E. Levinger, J. M. Papanikolas, and W. C. Lineberger, *J. Chem. Phys.* **91**, 6533 (1989).
6. J. J. Breen, L. W. Peng, D. M. Wilberg, A. Heikal, P. Cong, and A. H. Zewail, *J. Chem. Phys.* **92**, 805 (1990).
7. J. Steadman and J. A. Syage, *J. Chem. Phys.* **92**, 4630 (1990).
8. A. L. Harris, J. K. Brown, and C. B. Harris, *Ann. Rev. Phys. Chem.* **39**, 341 (1988) and references therein.
9. E. M. Kosower and D. Huppert, *Ann. Rev. Phys. Chem.* **37**, 127 (1986) and references therein.

7. High-Resolution Infrared Spectroscopy of Weakly Bonded Molecular Clusters

S. W. Sharpe

Small, weakly bonded clusters of molecules and atoms have found an important niche in experimental and theoretical chemical physics research. These systems are used to elucidate chemical reactions on a microscopic level, where the orientation and quantum states of the reactants are fully characterized.^{1,2} Clusters provide a unique opportunity to study energy transfer and internal vibrational relaxation (IVR) processes.^{3,4} In addition, small clusters (for example, H₂O-H₂O) contribute to the atmospheric radiation balance and may play an important role in global warming.⁵

Regardless of the chemical identity, it is the hydrogen bond and the van der Waals or dispersive forces that are primarily responsible for the characteristics of

these clusters. Fundamental, quantitative knowledge about the nature and consequences of these long-range intermolecular forces can be obtained from the spectroscopy of such clusters, in which the weak, anisotropic interactions that dictate dynamics and geometry are often exposed in the form of rich and varied signatures.

Researchers have a number of techniques that can be used to "examine" small clusters. Although mass, electronic, and electron diffraction spectroscopies are all powerful techniques, microwave and infrared (IR) spectroscopies are unsurpassed in their ability to obtain high spectral resolution and accurate data.

One particularly promising IR technique for exploring the 300 to 2400 cm⁻¹ region uses rapidly tunable diode lasers and pulsed, slit, supersonic expansions. This "fast-scan" technique, developed by DePiante et al.⁶ and Sharpe et al.,⁷ offers rapid data acquisition, high sensitivity, high resolution, continuous coverage, and, most importantly, access to the majority of vibrational motions including intramolecular bending modes. A representative spectrum (for example, CO₂-Ar) taken in less than two-thousandths of a second using the fast-scan technique is shown in Figure 7.1.

Detailed results from one of these IR studies, involving the CO₂-HX (HX = HF, HCl, and HBr) clusters, revealed several important trends. Specifically, hydrogen bond and dispersive forces are in "competition" and the "winner" dictates the structure of the cluster. Additionally, subtle changes in these molecules can lead to profound dynamical effects; for example, the lifetimes of the vibrationally excited state differ by an order of magnitude for the deuterated versus undeuterated complex.⁷

Spectra corresponding to CO₂-HX (HX = HF, DF, H^{35,37}Cl, D³⁵Cl, and HBr) were recorded in the 4.5-μm region (for example, the asymmetric stretch of CO₂) and analyzed.⁷ Both the HF(DF) and HCl(DCl) spectral patterns consist of simple P and R transition series, indicative of a linear rotor (Figure 7.2). Both spectra also show a second series of transitions composed of doublets, indicative of a linear molecule undergoing an internal vibrational motion (for example, intermolecular degenerate bend) or an asymmetric rotor with K_a ≠ 0. If the linear rotor scenario is invoked, a bending frequency of 10 cm⁻¹ can be calculated, while an asymmetric rotor model predicts a rotational constant of 7 cm⁻¹. The origin of the doublets may be a semantical point since the energy of the intermolecular

Figure 7.1. Fast-scan technique used to record part of the infrared spectrum of $\text{CO}_2\text{-Ar}$. Rapidly tuned laser light passes through the effluent of a pulsed supersonic ribbon of gas. Clusters are created in the expansion, which lasts for two-thousandths of a second, and absorb the laser light. By plotting laser attenuation versus laser frequency, a direct absorption spectrum is produced. Vibrational excitation corresponds to the intramolecular asymmetric stretch mode of CO_2 ($4.5\ \mu\text{m}$).

vibrations and rotations are both the same. It is clear that conventional Hamiltonians (i.e., Watson Hamiltonian) do not adequately describe these systems, which require vibrational-rotational and internal angular momentum coupling terms.

Unlike $\text{CO}_2\text{-HF}$ and $\text{CO}_2\text{-HCl}$, spectral analysis of $\text{CO}_2\text{-HBr}$ strongly indicates an asymmetric rotor (see Figure 7.3). $\text{CO}_2\text{-HBr}$ is a T-shaped cluster with bromine directly below the carbon of OCO (see Figure 7.4). Prior to these experiments, and in the tradition of keeping with $\text{CO}_2\text{-HF}$ and $\text{CO}_2\text{-HCl}$, it had tacitly been assumed that $\text{CO}_2\text{-HBr}$ was also linear.

In retrospect, these results are consistent with what is known about long-range forces. Reed et al. recently carried out extensive *ab initio* calculations based on natural bond orbital analysis (NBO), where emphasis

Figure 7.2. Typical spectrum of the $\text{CO}_2\text{-HCl}$ clusters taken by averaging 200 gas pulses. The most intense peaks are due to the ^{35}Cl isotope, while the weaker transitions (to the red) correspond to the ^{37}Cl isotope. Notice the CO_2 reference spectrum, used for absolute frequency calibration. Vibrational excitation corresponds to the intramolecular asymmetric stretch mode of CO_2 ($4.5\ \mu\text{m}$).

Figure 7.3. A small region of the infrared spectrum corresponding to T-shaped $\text{CO}_2\text{-HBr}$ (250 averages). Notice the expanded frequency scale, relative to Figure 7.2. Etalon trace used for relative frequency calibration. Vibrational excitation corresponds to the intramolecular asymmetric stretch mode of CO_2 ($4.5\ \mu\text{m}$).

a) Linear $\text{CO}_2\text{-HF(HCl)}$

b) Bent $\text{CO}_2\text{-HBr}$

Figure 7.4. Pictorial representation of linear $\text{CO}_2\text{-HF(HCl)}$ and bent $\text{CO}_2\text{-HBr}$.

is placed on charge-transfer interactions.⁸ With NBO, each subunit (for example, CO_2 and HX) is described in terms of a set of orthonormal bond orbitals. The lower filled set of orbitals corresponds to the usual Lewis structure including core, bonding, and lone pairs of electrons. The higher unfilled orbitals are associated with antibonding and Rydberg-like orbitals. In this analysis, charge transfer is treated by allowing electron density to shift from the filled orbitals of one subunit (for example, CO_2) to the "unfilled" orbitals of the second subunit (for example, HX). Reed et al. found that many of the complexes modeled had two minima—one corresponding to a hydrogen-bonded species and the other belonging to a non-hydrogen-bonded species. In this respect, HF and HCl are potent σ^* acceptors, preferring linear O-H bonded structures over the asymmetric C-X bonded species that require the halogen atom to act as a base.

Besides gross structural changes, large dynamical effects are also observed between slightly different clusters. A comparison of the $\text{CO}_2\text{-HF}$ and $\text{CO}_2\text{-DF}$ spectral linewidths reveals the former to be about five times broader than the latter. A representative spectrum for a single rovibrational line of both clusters is shown in Figure 7.5 and indicates predissociative lifetimes of 0.9 ns and 6 ns for $\text{CO}_2\text{-HF}$ and $\text{CO}_2\text{-DF}$, respectively. Similar results are also observed for the $\text{N}_2\text{O-HF}$ and $\text{N}_2\text{O-DF}$ clusters.⁹ It has been suggested

Figure 7.5. Linewidth data for $\text{CO}_2\text{-HF}$ and $\text{CO}_2\text{-DF}$ taken on a single-shot basis. Deconvolution of the Voight profile, with a 20-MHz heterogeneous (Doppler) linewidth, corresponds to vibrationally excited lifetimes of 0.9 and 6 ns for $\text{CO}_2\text{-HF}$ and $\text{CO}_2\text{-DF}$, respectively. Vibrational excitation corresponds to the intramolecular asymmetric stretch mode of CO_2 ($4.5 \mu\text{m}$).

that the lighter HF particle, upon dissociating, has rotational resonance channels available that are not available to the heavier DF particle. Further investigation will be required before the origin of these dynamical effects can be adequately explained.

For several decades it has been known that the earth's atmosphere is transparent in the 8- to $13\text{-}\mu\text{m}$ region, except over large bodies of water and in tropical climates, where attenuations of up to 50% have been noted. This anomalous absorption in the IR atmospheric window is characterized by a broad, featureless continuum. While both molecular H_2O and CO_2 are the only species that are sufficiently abundant and infrared active, neither exhibits a continuum spectrum. "Wing" and "dimer" models have been developed to explain this anomalous absorption. The wing model attributes the continuum to overlapping wings of homogeneously (for example, pressure) broadened absorption due to microwave and IR transitions of CO_2 and/or H_2O . The dimer model attributes the

continuum to the IR absorption of water dimers (for example, $\text{H}_2\text{O}-\text{H}_2\text{O}$). Presently, there is no conclusive evidence for choosing one model over the other.

In an effort to resolve and elucidate the wing versus dimer conflict, research is underway to spectroscopically investigate water clusters using a tunable (for example, $\Delta\nu = 350$ MHz) CO_2 waveguide laser and molecular beam bolometry. In parallel, Watts and coworkers are developing Monte Carlo simulations that will help locate IR vibrations of the water clusters.¹⁰ In addition, a fast-scan facility is currently under development at the MSRC and will cover the entire atmospheric window. Unlike previous systems, this machine will produce very high densities of ultracold clusters and ultimately be capable of covering a large portion of the infrared (for example, 300 to 3500 cm^{-1}).

References

1. C. Wittig, S. Sharpe, and R. A. Beaudet, *Acc. Chem. Res.* **21**, 341 (1988).
2. C. Jouvet and B. Soep, *Chem. Phys. Lett.* **96**, 426 (1983).
3. R. E. Miller, *J. Phys. Chem.* **90**, 3301 (1986).
4. G. E. Ewing, *J. Phys. Chem.* **91**, 4662 (1987).
5. J. T. Houghton, *The Physics of Atmospheres*, Cambridge University Press, 1986.
6. A. DePiante, E. J. Campbell, and S. J. Buelow, *Rev. Sci. Instr.* **60**, 858 (1989).
7. S. W. Sharpe, Y. P. Zeng, C. Wittig, and R. A. Beaudet, *J. Chem. Phys.* **92**, 943 (1990).
8. A. E. Reed, F. Weinhold, L. A. Curtiss, and D. J. Pochatko, *J. Chem. Phys.* **84**, 5687 (1986).
9. Y. P. Zeng, S. W. Sharpe, D. Reifschneider, C. Wittig, and R. A. Beaudet, *J. Chem. Phys.* **93**, 183 (1990).
10. J. R. Reimers and R. O. Watts, *J. Chem. Phys.* **85**, 83 (1984).

Environmental Dynamics and Simulation

Environmental Dynamics and Simulation

The Environmental Dynamics and Simulation (EDS) work combines expertise from PNL's Earth and Environmental Sciences Center with programs funded through the Environmental Science Research Center initiative and other sources. The EDS program addresses fundamental problems in the restoration of contaminated subsurface regions. This work will eventually be part of the Environmental and Molecular Sciences Laboratory (EMSL) and is closely related to the five MSRC research programs.

In the EDS program, basic research is used to develop innovative remediation concepts by understanding 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 the ability to predict contaminant form and movement and to devise remedial cleanup measures for contaminated environments. Thus, the focus of the EDS program is macroscopic, microscopic, and molecular-level understanding of the reactions between environmental contaminants and geological materials that occur at the solid/liquid interface.

The Environmental Dynamics Laboratory will be equipped to directly measure aqueous speciation of solutes and the bonding environment and speciation of sorbed solutes in colloidal suspensions. Evaluating 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. This linkage will allow 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.

Work in the areas of quantum chemistry of clay minerals and synchrotron development is described in the following sections.

1. Quantum Chemistry of Clay Minerals

C. J. Hostetler and L. J. Criscenti

The first research program initiated in the EDS program involves calculating the electronic properties of the ring structures in clay minerals. This work is being done in concert with staff in the Theory, Modeling, and Simulation program (see p. 49 for more information).

In subsurface materials, clay minerals act to adsorb contaminants from solution, thus attenuating aqueous concentrations. This research is aimed at quantifying the interactions among clay mineral substructures and solute species.

Atomic positions for the unit cells of kaolinite, gibbsite, and pyrophyllite were found from literature descriptions of x-ray and neutron diffraction studies. Positions for the hydrogen atoms were not available for the kaolinite structure, so the hydrogen positions from pyrophyllite were used as an analog.

Calculations were made using the CRYSTAL¹ computer program, which implements a periodic spin-restricted Hartree-Fock algorithm. The calculations showed that the ring structure of kaolinite has a slightly positive electrostatic potential and low electron density. The calculations will be repeated for the pyrophyllite structure to investigate if the substitution of aluminum into the ring structure will increase the electronic density associated with the ring structure.

Reference

1. R. Dovasi, C. Pisani, C. Roetti, M. Causa, and V. R. Saunders, *Quantum Chemistry Program Exchange*, Publication 577, University of Indiana, 1989.

2. Synchrotron Development

J. E. Amonette and S. V. Mattigod

An important aspect of the EDS 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. Kinetic studies with resolutions on the order of micro- and nano-seconds are possible.

Staff are currently participating in the Pacific Northwest Consortium proposal for the Advanced Photon Source at Argonne, Illinois, and have initiated proposals for exploratory work at the National Synchrotron Light Source at Brookhaven, New York.

Macromolecular Structure and Dynamics

Macromolecular Structure and Dynamics

The primary objective of the Macromolecular Structure and Dynamics program is to develop and utilize advanced spectroscopic techniques for analyzing the structure and dynamics of large macromolecules. This objective includes the design and development of leading-edge nuclear magnetic resonance (NMR) and mass spectrometry (MS) instruments that will have broad applicability to the analysis of molecular structures and dynamic processes relevant to biological and environmental science, chemistry, and materials science.

Using these instruments, high-resolution measurements can be made of primary, secondary, and tertiary structures of large proteins and nucleic acids. Other applications of these instruments include ultratrace analysis of components in complex chemical mixtures, gas-phase chemical dynamics, interfacial phenomena, ligand-receptor interactions, and spectroscopic imaging.

NMR spectroscopy has found wide applicability during the past decade for determining the three-dimensional (3-D) conformation of biological macromolecules, both in their native states and in perturbed states resulting from the interaction of environmental pollutants and other substances. Included in the NMR program plan is the development of a gigahertz spectrometer that will allow the structural analysis of large macromolecules that cannot be completely characterized by available spectroscopic techniques. For example, the gigahertz NMR spectrometer is expected to provide new capabilities for investigating the structures of biodegradative enzymes and a variety of large proteins that are involved in the regulation of cell and tissue growth in normal and cancerous states.

The MS technique has experienced a virtual revolution during the past decade as a result of innovations such as electrospray ionization (ESI), which extends the size of the macromolecules that can be studied by two to three orders of magnitude. In addition, chromatographic and electrophoretic preseparation techniques have been successfully interfaced with MS instruments for analysis of chemical species in complex mixtures. Another major advance has been the introduction of photodissociation and collisional dissociation techniques in tandem with MS, thereby enabling sequencing to be done on large proteins and nucleic acids. These developments have made MS a highly versatile

technique that is widely applicable to the analysis of biomolecular structures and studies of the interaction of biomolecules with toxic substances in the environment.

In the following sections, the activities during the past year in the design of the first gigahertz NMR spectrometer and in the development of large molecule MS capabilities are described.

1. Preliminary Design of a Gigahertz NMR Spectrometer

T. S. Tenforde

High-field multidimensional nuclear magnetic resonance (NMR) spectroscopy has become a widely used technique for determining the aqueous-phase three-dimensional (3-D) structures of biological macromolecules in their native states and in highly perturbed states due to the interaction of drugs, chemical mutagens, and other substances. A major goal of the NMR program within the MSRC will be to develop the first gigahertz NMR instrument and support facilities. This instrument, when used in combination with new 2-D, 3-D, and 4-D NMR techniques, will enable a complete structural analysis to be performed on large macromolecules that cannot be characterized by existing spectroscopic techniques.

The gigahertz spectrometer will offer distinct advantages over existing NMR spectrometers that operate at frequencies up to 600 MHz. For example, the size of proteins for which secondary and tertiary structure information can be obtained will be increased significantly above the current limit of approximately 20 kDa. The secondary and tertiary structures can be analyzed in oligonucleotide sequences that contain as many as 40 base pairs, which would represent a significant advance for characterizing sequence-dependent local variations in DNA structures that are important factors in the interaction of proteins, drugs, and chemical mutagens with DNA. The quantities of proteins and nucleic acids required to obtain interpretable NMR spectra will be reduced significantly as a result of the increased signal detection sensitivity of a gigahertz spectrometer.

In addition to its applicability to structural studies on biomolecules, the gigahertz spectrometer would be useful in materials science problems that rely on high NMR sensitivity and resolution. For example, studies on quadrupolar nuclei and nuclei with small gyromagnetic ratios would be facilitated. In addition, the prospects for spectroscopic imaging of small samples would be enhanced by the high-field capabilities of a gigahertz NMR system.

The scientific advantages and technical feasibility of developing a gigahertz NMR spectrometer were explored in two workshops:

- *High-Field NMR and Biological Applications*, held at PNL on September 8-9, 1989¹
- *Workshop on the Development of a Gigahertz NMR Spectrometer*, held at the Battelle Conference Center, Seattle, Washington, March 8, 1990 (proceedings is being prepared).

In the first workshop, several conclusions relating to the scientific advantages and technical obstacles of developing the gigahertz instrument were reached. First, recent experience with 600-MHz NMR spectrometers in several laboratories has shown a significant improvement in resolution and sensitivity over conventional 500-MHz instruments. As a result, a considerable increase in spectral resolution is anticipated for large macromolecules at frequencies approaching 1 GHz.

Second, achieving sufficient field homogeneity for NMR at field levels above 20 tesla represents a significant technical problem. Recent advances have been made in this area, and a prototype magnet designed to achieve 21.1 tesla at 1.8K with adequate uniformity for NMR has been completed by scientists at Intermagnetics General Corporation and Carnegie-Mellon University. A field level of close to 21 tesla was reached in tests of this magnet conducted at the Lawrence Livermore National Laboratory.

Third, magnetic orientation effects and chemical shift anisotropy cause significant line broadening at very high field levels, which can be overcome to some extent by optimization of pulse sequences. Fourth, novel multiple-pulse sequences are needed at very high frequencies to preserve spin magnetization transfer information, and progress is being made in this area.

Fifth, the extent of penetration of radio frequency (RF) pulses and the degree of sample heating in a gigahertz NMR spectrometer should not pose insurmountable technical difficulties.

The second workshop involved 27 participants from universities, national laboratories, and industry who are specialists in the fields of superconducting materials, high-field magnet design, RF systems, NMR console design, and data acquisition and analysis systems. The general conclusion and recommended course of action that emerged from this workshop was that the development of a gigahertz NMR spectrometer should proceed by a sequential approach in which the spectrometer magnet system is designed from the outermost coils towards the innermost high-field coils.

Using this approach, the outer two sets of magnet coils would be composed of NbTi and Nb₃Sn, respectively; and the innermost coils would be added last using available state-of-the-art superconducting materials. Several new superconducting materials, including (Nb,Ta)₃Sn and (Nb,Ti)₃Sn, are capable of carrying a current density of several thousand amperes per square centimeter at field levels above 20 tesla. These materials have previously been proposed for the innermost high-field coils of a 21.15-tesla magnet for proton NMR at 900 MHz.

Following the March 1990 workshop, five subcontracts were established with various organizations to produce a preliminary design of a gigahertz NMR spectrometer and to provide pertinent information on superconducting materials and magnet technology. Two of the subcontractors (Wang NMR and Intermagnetics General Corporation) who have designed 900-MHz spectrometers were asked to extend these designs to a gigahertz system. The other three subcontractors were requested to provide the following: a status report on available superconducting materials suitable for developing a gigahertz NMR spectrometer (Lawrence Berkeley Laboratory), console design and computing requirements (Carnegie-Mellon University), and oversight and synthesis of the gigahertz spectrometer design options (Massachusetts Institute of Technology National Magnet Laboratory). The final reports of these subcontractors were received by August 1990. The information contained in these reports related to superconducting materials, high-field magnet technology, and the gigahertz NMR spectrometer preliminary design is briefly summarized in the following sections.

Superconducting Technology

Based on a literature review and responses to a questionnaire that was sent to leading international superconductor manufacturers and research groups, it was concluded that there are several candidate conductors for the high-field coils of the gigahertz spectrometer magnet. When operated at 1.8K, the current density capability of $(\text{Nb,Ta})_3\text{Sn}$ and $(\text{Nb,Ti})_3\text{Sn}$ conductors is at least 3 kA/cm², and possibly as high as 10 kA/cm², at a field level of 22 to 24 tesla. This feature makes Ta- or Ti-doped niobium tin superconductors possible candidates for the inner high-field coils of the 23.5-tesla magnet.

Other new superconducting materials such as Nb_3Al , $\text{Nb}_3(\text{Al,Ge})$, and Chevrel phase materials (for example, PbMo_6S_8) are even more promising than the Ta- or Ti-doped niobium tin conductors in terms of current density capability. In addition, these superconductors have a better strain tolerance at field levels above 20 tesla. However, the production of these new materials in long lengths of uniform conductor suitable for a gigahertz spectrometer magnet has not been accomplished to date; Ta- or Ti-doped niobium tin conductors over 1 km long have been fabricated and tested successfully.

Magnet Design

Preliminary designs for the 23.5-tesla magnet involving arrays of up to 11 superconducting coils incorporate an outermost notched NbTi superconductor for eighth-order field corrections and a superconducting Nb_3Sn shim coil located in the intermediate field region. This shim coil and the resistive shim coil in the magnet bore must be able to provide field uniformity at the sample of better than 1 ppb.

Extensive analyses were made of field uniformity, the magnet's stored energy, cryostat design and cryogen loss rate, mechanical stresses, quench protection, and fringe fields. The modular design of the magnet will permit the outer NbTi and Nb_3Sn conductors to be operated in a persistent mode, while the inner high-field coils can be operated in a driven mode (if that is required for achieving and maintaining the target current density).

The large mechanical stresses in the high-field magnet region (~250 MPa) do not pose a serious technical problem in relation to operational safety or effects on current density in the high-field superconductors. The calculated fringe field profile places the 5-gauss level at a radial distance of about 10 m from the magnet's geometric center, which will necessitate shielding in the laboratory containing the gigahertz spectrometer.

Other Spectrometer Design Features

For multidimensional heteronuclear NMR applications, the spectrometer RF system and probes will have the capability for coordinated measurements on three species of nuclei. For protons and other nuclei in spinning samples, the resolution must meet the requirement that the linewidth at half peak height is less than 0.2 Hz. The data analysis requirements for this system will be extensive, especially for 3-D and 4-D spectra, and will necessitate supercomputer capabilities and high-speed workstations.

Future Program Direction

Initial work on the design and fabrication of the gigahertz NMR spectrometer will be undertaken in late 1990. The first phase of this work will involve tests of the candidate superconducting materials for the innermost high-field magnet coils. A contract for these studies will be awarded to a commercial vendor by March 1991. The second phase will involve the design and fabrication of the 23.5-tesla magnet for the gigahertz spectrometer. The contract for this work will be awarded in early 1992. Future work leading to completion of the gigahertz spectrometer involves design and fabrication of the RF system and console, procurement of a data analysis computer, and system integration and testing.

Reference

1. T. S. Tenforde (ed.), *Proceedings of the Workshop on High-Field NMR and Biological Applications* (Richland, Washington, September 8-9, 1989), PNL-SA-18016 (CONF-8909305), Pacific Northwest Laboratory, Richland, Washington, 1990.

2. Large Molecule Mass Spectrometry

R. D. Smith, J. A. Loo, A. L. Rockwood, and H. R. Udseth

Mass spectrometry (MS) is playing an increasingly important role in environmental, health, and biochemical research. The aim of studies being conducted at PNL is to extend MS into new realms of sensitivity and applicability to large molecules. In the Large Molecule Mass Spectrometry (LMMS) program, new instrumentation and methods are being developed that will extend MS into the regime of large molecules and small particles.

The LMMS research has involved both fundamental and applied aspects. The primary methods being explored are based on electrospray ionization (ESI); PNL has played a key role in its development. A goal has been the development of ultrasensitive analytical methods appropriate for environmental applications and as tools to probe molecular species at solid and liquid interfaces. The ESI method has been used as the basis for coupling new capillary electrophoresis (CE) separation methods amenable to complex environmental or biological mixtures with very high sensitivities (10^{-18} -mole detection limits have been demonstrated in experiments to date).

The combination of high-resolution separation methods with LMMS, necessary for application to many environmental and biological systems, is being developed to characterize previously intractable mixtures. Potential applications resulting from these new developments may include much more sensitive methods for sequencing biopolymers (for example, proteins and oligonucleotides) and highly sensitive analytical methods to support environmental- and health-related research.

Electrospray Ionization Process

Although the use of ESI for MS is relatively recent, it and related phenomena have been extensively investigated. ESI production requires two steps: dispersal of highly charged droplets at near-atmospheric pressure followed by conditions resulting in droplet evaporation.

An electrospray is generally produced by application of a high electric field to a small flow of liquid (generally 1 to 10 $\mu\text{L}/\text{min}$) from a capillary tube. A potential

difference of 3 to 6 kV is typically applied between the capillary and the counter electrode located 0.3 to 2 cm away (where ions, charged clusters, and even charged droplets, depending on the extent of desolvation, may be sampled by the MS through a small orifice). The electric field results in charge accumulation on the liquid surface at the capillary terminus; thus, the liquid flow rate, resistivity, and surface tension are important factors in droplet production.

The high electric field results in disruption of the liquid surface and formation of highly charged liquid droplets. Positively or negatively charged droplets can be produced depending on the capillary bias. The use of only electric fields for nebulization leads to some practical restrictions on the range of liquid conductivity and dielectric constant. Solution conductivity of $\leq 10^{-5}$ S is required at room temperature for a stable electrospray at useful liquid flow rates, corresponding to an aqueous electrolyte solution of $\leq 10^{-4}$ M.

Most stable electrospray performance is generally obtained when the current due to ion migration to the liquid electrospray tip is well matched to electrolyte concentration. Fluids with higher surface tensions require a higher threshold voltage for stable electrospray production (~ 8 kV for water versus ~ 4 kV for methanol given a 1-cm capillary/counter electrode distance). Higher dielectric liquids produce higher currents.

While ESI currents for a typical water/methanol/5% acetic acid solution would be in the range of 0.1 to 0.5 μA , conducting liquids can produce much higher ESI currents (up to 500 μA for liquid metals). For conducting liquids, stable operation is obtained under very low flow rate conditions, where droplet production is minimized and direct field-induced ion evaporation apparently dominates.

In the mode found most useful for ESI-MS, an appropriate liquid flow rate results in dispersion of the liquid as a fine mist. A short distance from the capillary the droplet diameter is often quite uniform and on the order of 1 μm . Of particular importance is that the total ESI current increases only slightly for higher liquid flow rates. Increasing flow rates result in formation of larger droplets and ultimately electrical breakdown, although the use of a nebulizing gas can produce stable results at flow rates as high as 100 $\mu\text{L}/\text{min}$. The use of higher voltage does not substantially increase the ESI current until the onset of a corona discharge (generally at >6 kV).

The formation of molecular ions requires conditions effecting evaporation of the initial droplet population. This can be accomplished at higher pressures by a flow of dry gas at moderate temperatures ($<60^{\circ}\text{C}$), by heating during transport through the interface, and (particularly in the case of ion-trapping methods) by energetic collisions at relatively low pressure. Droplets shrink to the point where repulsive Coulombic forces approach the level of droplet cohesive forces (for example, surface tension).

Two mechanisms can be suggested for ion formation from charged droplets: droplet fission at the Rayleigh limit and direct field evaporation of ions. A field of $\sim 10^8$ V/m is required for evaporation of "preformed" ions, as opposed to the larger field strengths required for desorption ionization of neutral species from solution. The maximum droplet charge is proportional to the $d^{3/2}$ (d = droplet diameter) for Rayleigh fission and d^2 for direct ion evaporation.

For large ($>1\text{-}\mu\text{m}$) droplets, there is no doubt that the Rayleigh limit applies. Droplets explode, typically shedding more than 10% of their charge and about an order of magnitude less mass. Thus, it has been postulated that droplets undergo a cascade of fission processes, yielding smaller and smaller droplets until the electric field at the droplet surface is sufficient for ion evaporation.

The very small droplets produced by ESI appear to allow almost any species carrying a net charge in solution to be transferred to the gas phase after evaporation of residual solvent. The wide range of solutes already found to be amenable to ESI-MS and the lack of substantial dependence of ionization efficiency upon molecular weight suggest a highly nondiscriminating and broadly applicable ionization process.

Two factors make ESI of intense interest. First, very large molecules can be ionized (at least 5 million dalton) as intact positive or negatively charged molecular ions (with charge states extending up to at least several thousand). Second, extremely good detection limits can be obtained for charge species in solution.

ESI-MS Sensitivity of Detection for Macromolecules

A 10^{-4} M analyte solution of a singly charged species can account for the total ESI current at a flow rate of $1\text{ }\mu\text{L}/\text{min}$. Higher concentrations of electrolytes appear

to "saturate" the mass spectrum and displace "normal" solvent-related peaks at low mass-to-charge ratio (m/z). If the analyte carries more than one charge, the concentration that will saturate the ESI process decreases proportionately. Concentrations as low as 10^{-10} M (or $\sim 10^{-18}$ mol/s) of singly charged species will give detectable ion currents (~ 10 counts/s) using a conventional quadrupole MS if the analyte is completely ionized.

Although efficient sample utilization will ultimately require advanced sample-handling techniques, such as those based on CE, remarkably little sample is actually consumed in obtaining an ESI mass spectrum. Figure 2.1 gives ESI mass spectra obtained for aqueous solutions of horse heart cytochrome c (molecular weight [MW] 12,360) prepared in 5% acetic acid introduced at 0.5 to $1\text{ }\mu\text{L}/\text{min}$ using the sheath flow ESI source. Spectra were acquired in 90-s scans for solution concentrations ranging from 1.5×10^{-4} M (Figure 2.1a) to 1.5×10^{-8} M (Figure 2.1f). It should also be noted that $>95\%$ of the sample is deposited on a small spot near the sampling orifice and can be efficiently recovered by rinsing the sample off a small foil disk attached to the surface around the sampling orifice. For the most dilute solution, a spectrum of quality adequate for MW determination required only 23 fmol ($1\text{ fmol} = 10^{-15}\text{ mol}$) of cytochrome c, while less than 1 fmol was actually consumed. Improved inlets and instrumentation should reduce this requirement to low attomole (10^{-18} M) quantities.

Mass spectra are dominated by the distribution of multiply protonated molecular ions, but other contributions are also evident. For example, Figure 2.1b shows a scale expansion (X36) for the most concentrated solution (Figure 2.1a). The spectrum shows a number of small peaks between m/z 550 and m/z 850 that may be due to small contributions of collision-induced dissociation (CID) in the nozzle-skimmer interface from the most highly charged species. Small contributions that correspond to multiply charged dimers are also evident.

For cytochrome c concentrations below $\sim 2 \times 10^{-5}$ M, two additional observations pertain. First, the relative intensities of higher charge states increase and become nearly independent of solution concentration. Second, the lower charge states show contributions of adduct ions (98 ± 2 amu), giving a series of small peaks on the high m/z side of the molecular ions. At lower cytochrome c concentrations, the relative size of these adduct contributions is nearly constant. This is fortunate since the assumption that the dominant species

a)

b)

c)

d)

e)

f)

Figure 2.1. ESI-MS spectra of cytochrome c obtained at sample flow rates of $0.5 \mu\text{L}/\text{min}$ for solutions of $1.5 \times 10^{-4} \text{ M/L}$ to $1.5 \times 10^{-8} \text{ M/L}$, consuming from 230 pmol (2.1a) to 23 fmol (2.1f) during a 90-s scan. Scale expansions are shown in 2.1b and 2.1d for the spectra in 2.1a and 2.1c.

are due to molecular ion protonation remains valid at very low sample concentration.

Peak intensities for the lower charge states increase nearly linearly with sample concentration. This behavior suggests that high sample concentrations result in formation of ions with reduced charge states, rather than lower ionization efficiency. Thus, although the peak intensity for the most abundant charge state is "saturated," a nearly linear correlation between peak intensity and concentration is still obtained for the lower charge states. This can actually result in a decrease in detected ion abundance for very high protein concentrations.

One of the most striking aspects of the ESI process is that it appears to approach unit ionization efficiency. For example, in Figure 2.1f, cytochrome c molecular ions reach the detector at a rate of $\sim 3000/\text{s}$ if all peaks are summed. The flow rate to the ESI source is $2.7 \times 10^{-16} \text{ mol/s}$. Thus, the overall efficiency is 1.8×10^{-5} , very close to the measured efficiency of ion transmission and detection. Although more efficient transmission of large ions might contribute to this observation, it seems clear that ionization efficiency must be very high.

Even at *present levels* of instrument performance, it is conceivable that useful spectra of small proteins such as cytochrome c might be obtained with as little as 1 fmol. Substantial gains might also be obtained by the use of array detectors with magnetic electrostatic sector instruments, allowing simultaneous detection of portions of the spectrum.

The "background" in Figure 2.1f is probably due to trace impurities (in solvents, on capillary surfaces, etc.). The actual detector "noise" amounts to <4 counts/s. Thus, a more limited scan range (for example, m/z 600 to 1000) and reduced background might accomplish this goal. However, such a situation would be realistic only for very clean samples (unlikely for "real-world" applications) or with online sample cleanup and separation (using a technique such as CE). Since currently only $\sim 10^{-5}$ of all ions formed by ESI are detected, attention to the factors limiting instrument performance should provide a basis for a substantial extension of ESI-MS sensitivity.

Useful ESI-MS for very large proteins will require both more efficient ion utilization and resolution. Instrumentation being developed for the EMSL will also incorporate features that allow ion charge states

to be determined. PNL studies with proteins of MW above 200,000 have produced spectra with an unresolved "hump," consistent with the limitations of current instrumentation. Finally, the sample concentration necessary to saturate the ESI peak intensity decreases nearly linearly with the average charge state, from $\sim 10^{-4} M$ for a singly charged species to $10^{-6} M$ for a protein of MW 100,000 with an average of ~ 100 charges/molecule. Thus, if one assumes a charge distribution centered around m/z 1000, an efficiently ionized protein will saturate the ESI signal at a sample concentration of $\sim 0.1 \mu\text{g}/\mu\text{L}$ for a $1\text{-}\mu\text{L}/\text{min}$ flow rate regardless of MW.

Proteins in excess of MW 100,000 are amenable to ESI-MS with conventional quadrupole instruments due to the multiple-charging phenomenon. The relationship between MW and maximum observed charge state for polypeptides and proteins studied to date is shown in Figure 2.2. A similar correlation exists between the total number of basic amino acid residues (lysine, arginine, histidine, plus one for the N-terminus) and the maximum number of positive charges observed for smaller proteins. However, many proteins contain disulfide bridges in their native structure that

Figure 2.2. Maximum charge observed by ESI-MS versus MW for a variety of polypeptides and proteins. The effect of reduction of disulfide linkages is shown by arrows for bovine albumin (MW 66,300) (A) and bovine albumin dimer (MW 133,000) (B).

significantly affect higher-order (secondary, tertiary) structure. Reduction of disulfide bonds with 1,4-dithiothreitol (Cleland's reagent) results in more highly charged molecular ions. These experiments demonstrate the capability of using ESI-MS to probe higher-order protein structures.

ESI-Tandem MS of Biomolecules

The major characteristics of ESI mass spectra for biomolecules are the predominance of multiply charged molecular ions and the lack of fragmentation. While this allows for accurate MW determinations, little information regarding molecular structure is obtained. Tandem mass spectrometry (MS/MS) of multiply charged ions produced by ESI is currently being explored to determine the extent to which sequence information for peptides and proteins can be obtained.

Probably the most dramatic examples of the efficient CID obtainable for multiply charged ions are for large proteins such as albumin. For such species, the molecular ion internal energies required for dissociation on the time scale of quadrupole instruments ($<10^{-3}$ s) are estimated to be about a few thousand electron volts. The ESI-CID mass spectrum of bovine serum albumin (MW 66,266) shows dissociation products evident in the m/z 500 to 1100 region.

For the large majority of CID studies of large peptides and proteins to date, dissociation occurs primarily near the termini of the polypeptide chain. Furthermore, fragment ions are unlikely to originate from within regions tied together by disulfide bridges since the probability of cleaving at least two bonds some distance from either terminus is very low.

Spectral interpretation with current instrumentation is facilitated by comparison of CID data from similar species. For example, because the sequences from bovine and human albumin show approximately 80% homology (sequence alignment) and because similar homology exists between the human and rat species, interpretation of major peaks becomes possible with

the assumption that fragmentation occurs in similar regions for each species, as shown in Figure 2.3.

Confidence in such assignments is raised by the observation of a series of multiply charged (3+ to 5+) "b" ions found in all three mass spectra, due to polypeptide backbone cleavages at amino acid residues 20-32 from the NH_2 -terminus. Out of the first 32 residues of bovine and human albumin, 5 are different, consistent with the observed m/z shift in the fragmentation patterns. A series of 3+, 4+, and 5+ sequence ions are detected for bovine and rat albumin, while the 5+ ion series is missing in the human albumin mass spectrum. The variation of residue 18, from a potentially protonated histidine residue (bovine, rat) to asparagine (human), is consistent with this difference.

The possibilities of MS/MS of multiply charged ions have only begun to be explored. Methods for circumventing the difficulties in assigning the charge state of fragment ions (and hence the mass) are needed, but more direct methods of charge-state assignment would provide a significant advance for these methods. It now appears, however, that limited sequence-related information can be obtained for large proteins in a matter of minutes. Higher energy CID or alternative activation methods, such as photo- and surface-induced dissociation and sequential tandem MS methods (MS_n), should generate more sequence information from larger species. The most promising approach would seem to involve the high-resolution capability of Fourier transform ion cyclotron resonance-MS with sequential laser photodissociation. Such an approach may provide a basis for the complete and rapid sequencing of intact proteins.

The advanced instrumentation being developed for the Environmental and Molecular Sciences Laboratory will provide new capabilities. Among the exciting possibilities is the study of the dynamics and reaction processes for individual large ions. Potential new capabilities include methods for sequencing the human genome based on sequential dissociation of single trapped molecular ions.

Figure 2.3. ESI mass spectra of bovine (top), human (middle), and rat serum albumin (bottom) (nozzle skimmer bias = +335 V), displaying fragmentation induced in the atmospheric pressure/vacuum interface. CID product ions are labeled with conventional notation, augmented with a superscript denoting the positive charge state.

Materials and Interfaces

Materials and Interfaces

Materials play a vital role in resolving many environmental issues. An in-depth understanding of how materials interact with their environment is necessary to develop permanent, defensible solutions to hazardous waste cleanup and disposal. Understanding molecular-level interactions of materials and their interfaces is required to guide the development of sensors, catalysts, separations membranes, containment and barrier materials, and contaminant transport models. These specialized materials and models are needed to characterize and minimize hazardous waste in complex environments as well as to permanently contain and dispose of the hazardous waste safely.

The MSRC Materials and Interfaces program is conducting basic research to obtain a fundamental understanding of materials/environmental interactions relevant to hazardous waste cleanup, disposal, and remediation. Detailed research plans for this program are being developed. Although the overall scope of materials-related environmental issues is clear, the final focus of some program areas will be determined by a new MSRC Associate Director for Materials and Interfaces.

To help focus program development, the *Environmental Materials and Interfaces* workshop was held in Richland, Washington, on September 10-12, 1990. Workshop recommendations will help refine program directions and capabilities for the Environmental and Molecular Sciences Laboratory.

Based on the examination of general waste and environmental problems, three important areas of research have been identified for this program:

- interface structure and chemistry
- materials synthesis
- materials and interface stability.

Research has begun in two areas: studies of the structure and chemistry of oxides and mineral surfaces and the development of multicomponent solids nuclear magnetic resonance (NMR). These two topics are discussed in the following sections.

1. Structure and Chemistry of Oxides and Mineral Surfaces

*D. R. Baer, D. L. Blanchard, and
M. H. Engelhard*

Although experimental studies of metal and semiconductor surfaces are common, similar studies for oxides and minerals of interest in environmental chemistry are relatively uncommon. Efforts are being focused in two directions: 1) conducting experiments that assist in the verification and extension of theory to new model systems and 2) extending the methods of surface science to more complex and environmentally relevant systems.

The interrelationship between these two activities is shown in Figure 1.1. The diagram shows how basic studies on single crystal surfaces are related to complex natural systems. Although the direct relationship of single crystal studies to the natural environment is not straightforward, there is a direct link in both information and the important questions between each step in the path. It is also important that the research in each area be viewed as occurring in a parallel and not in a linear sequence.

Experimental studies on oxide and mineral single crystal surfaces were initiated in the MSRC in October 1989. Initial efforts have been directed in two areas: 1) measurements of oxide surface stability and structure and 2) an examination of the chemistry of adsorbates on calcite. Work in 1991 will focus on the formation of model oxide and mineral thin films and the examination of the oxide/solution interface.

Oxide Surfaces

Only a few studies of oxide surface structure have been attempted; and because of the simplicity of its structure, MgO has been examined the most. However, electron diffraction studies have sometimes indicated differing results, and they have generally disagreed with ion-based studies of the surface.

Surface Structure and Chemical Bonding

Experimental Systems to Understand Adsorption and Desorption Processes on Oxide and Mineral Surfaces

Figure 1.1. Path by which studies at single crystal surfaces relate to complex natural systems where environmental problems occur. Although there is a large gap between the metal and semiconductor surfaces that are well understood at a fundamental level and the natural systems of environmental interest, each step in the path has significant areas of overlap with adjacent steps.

In collaboration with workers at Montana State University, we completed a low-energy electron diffraction (LEED) study of the MgO (001) surface to determine how well current LEED analysis codes deal with the data, to obtain current data to compare with theoretical predictions, and to help sort out the different values of surface relaxation (movement of the outer plane of atoms toward or away from the bulk spacing) and surface distortion (rumple) found in the literature.

The cleavage surface of MgO maintains the general symmetry of the bulk material. Detailed analyses of pulsed-beam LEED data taken on freshly cleaved MgO (001) surfaces were used to determine the amount of surface relaxation (d_{12} in Figure 1.2) and the amount of surface distortion (Δ_1 in Figure 1.2). Our analysis indicated ≈ 0 relaxation and $\approx 5\%$ rumple.¹

The electronic structure and surface compositions of rutile oxides TiO_2 and SnO_2 have been studied in the last few years. However, only a few surfaces have been found to be stable, and no surface structure measurements have been made.

In preparation for determination of surface structure for comparison with theoretical predictions, LEED symmetry and x-ray photoelectron spectroscopy composition studies of SnO_2 (111) and TiO_2 (110) and (001) surfaces were completed. The SnO_2 (111) surface

Figure 1.2. A side view of the MgO(001) surface. Pulsed beam LEED measurements were used to determine the amounts of surface relaxation (d_{12}) and differential relaxation or rumple (Δ_1).

maintained bulk symmetry over a wide range of temperatures and for considerable variation in the surface O-to-Sn ratio in contrast to the SnO_2 (110) surface, which exhibited a number of different structures (Figure 1.3). Electronic structure measurements for the (111) surface showed behavior similar to that reported in the literature for the frequently examined (110) surface. Both SnO_2 and TiO_2 surfaces will be subjected to LEED intensity-voltage studies in FY 1991.

Calcite Surfaces

The sorption of metallic cations on calcite is an important process that may control the concentrations of metal ions in ground water. Work by Zachara et al.² has shown significant differences in the sorption behaviors of various divalent cations on calcite. They postulated that two different sorption mechanisms must occur.

A new study of the calcite surface examines the nature of the adsorption of transition metals on a cleaved calcite surface. The natures of cleaved, sputtered, water-vapor-exposed, and water-immersed calcite surfaces were examined initially, followed by an investigation of the interaction of thin layers of Mn and Co with the calcite surface and the consequences of exposing these thin layers to water vapor and liquid. The differences in Mn $2p_{3/2}$ photopeak shape and line energy observed for a fraction of a monolayer of Mn freshly evaporated on calcite, the same surface after immersion in water, and metallic Mn are shown in Figure 1.4.³ The observed photopeaks are consistent with the substitution of Mn in the calcite lattice.

The comparison of the behavior of Mn and Co evaporated on the calcite surface will be completed in FY 1991, and a series of solution sorption studies will begin.

References

1. D. L. Blanchard, D. L. Lessor, J. P. LaFemina, D. R. Baer, W. K. Ford, and T. Guo, "A LEED Study of the MgO(001) Surface Structure," *J. Vac. Sci. Tech.* (in press).
2. J. M. Zachara, C. E. Cowen, and C. T. Rusch, "The Surface Exchange of Divalent Metallic Cations on Calcite," *Geochim. Cosm. Acta.* (in press).

a) (111) Surfaces

b) (110) Surfaces

Figure 1.3. Comparison of the variations in the oxygen-to-tin ratios and LEED patterns observed during the annealing of ion-bombarded SnO_2 . The (110) data are from D. F. Fox, T. B. Fryberger, and S. Semancik, *Surf. Sci.* **224**, 121-142 (1989).

Figure 1.4. Comparison of $\text{Mn } 2p_{3/2}$ photopeak locations and shapes observed for metallic Mn, Mn evaporated on calcite, and the same surface after immersion in water.

3. D. R. Baer, D. L. Blanchard, M. H. Engelhard, and J. M. Zachara, "The Interaction of Water and Mn with Surfaces of CaCO_3 : An XPS Study," *Surface and Interface Analysis* (in press).

2. Multicomponent Solids NMR Development

B. R. Stults, J. A. Franz, J. C. Linehan, and J. Schaefer^(a)

The solids nuclear magnetic resonance (NMR) project is designed to study the structure, bonding, and chemical reactions at solid/solid, solid/liquid, and solid/gas interfaces. The noninvasive element specificity of solids NMR is used to gain detailed molecular-level structural information at these hard-to-study solid interfaces. New instrumentation, new methodologies, and new theories are being developed to address the structural measurements on the molecular level.

^(a) Washington University, St. Louis, Missouri.

During FY 1989, this research was accomplished in collaboration with Professor J. Schaefer at Washington University, St. Louis, Missouri. Professor Schaefer and his postdoctoral and graduate students have performed the majority of the research in this project. A major goal has been the development of new instruments to be custom-built for the Environmental and Molecular Sciences Laboratory.

During FY 1990, the focus was on developing a new technique for measuring chemical specificity and bond distances at solids interfaces. This technique is referred to as Rotational Echo Triple Resonance (RETOR). It measures the weak dipolar coupling between rare spin nuclei, which provides a direct determination of distances between these rare spin nuclei up to 6 Å for elements such as carbon and phosphorous.

Two new four-resonance NMR probes were developed and tested. To establish the viability of the RETOR experiment for measuring dipolar couplings and distances in solids, tests were performed on a series of organic polymers with known crystal structures that had been selectively doped with rare spin nuclei at selected points.

Figure 2.1 illustrates the power of this technique as a series of spectra recorded for glyphosate labeled at specific sites with ^{15}N and ^{13}C . The structural formula for glyphosate is shown in Figure 2.1 along with a series of spectra. The spectra illustrate that the total ^{13}C spin echo NMR spectra can be recorded, showing all carbon atoms within the glyphosate molecules.

Using special NMR pulse sequences, we can selectively pick out those carbon atoms that are within 5 Å of a phosphorous atom and those that are within 5 Å of a nitrogen atom. Distances calculated from the NMR data for carbon phosphorous and carbon nitrogen distances compare favorably to the x-ray crystal structure to within ± 0.1 Å.

These experiments clearly demonstrate the potential of the RETOR technique to selectively measure structural parameters for specific elements that are close to nuclei that have been doped into the sample and have a proper spin to be detected by NMR.

The current focus of this work is to develop appropriate data deconvolution techniques to obtain structural parameters for those elements that are close to two rare spin nuclei. While obtaining structural information for a carbon atom that is close to only one rare spin nuclei is straightforward (i.e., either carbon

Figure 2.1. Spin echo ^{13}C spectra for labeled glyphosate in lysozyme (3 $\mu\text{mol}/250$ mg) showing the ability of selective NMR dephasing to isolate ^{13}C signals of interest.

phosphorous or carbon nitrogen distance in glyphosate), it is not straightforward to obtain information when the experiment involves dephasing for more than one nuclei to isolate the carbon atoms.

A prime goal of this research is to develop instrumentation and procedures to apply the RETOR technique to systems in which a metal atom has been doped into a solid matrix. For example, we are interested in measuring the bonding of platinum atoms that have been doped into selected coal samples to gain information about the metal bonding sites. Obtaining structural information on metal bonding sites in soils (clays) containing toxic metals such as cadmium and lead is also of interest.

Testing the RETOR technique for studies on platinum has involved the synthesis of special model compounds used to test our ability to measure distances between adsorbed metal atoms in a solid matrix. Several model compounds have been synthesized; and in one case, the crystal structure was determined using x-ray crystallography. However, initial experiments to obtain the RETOR data from the platinum samples were unsuccessful because the RF pulse sequences used in the

RETOR experiment use too much power, which completely "swamps" the signal from the carbon atoms.

To achieve the proper sensitivity to measure ^{13}C signals from carbon atoms close to elements such as platinum requires the development of a totally new scheme for pulse sequences. In this new scheme, the powerful $180^\circ \pi$ pulses will be replaced with a series of low-power RF pulses for platinum dephasing. The development of new pulse sequences and special data analysis procedures to deconvolute and quantify metal/carbon distances will be a major focus of work for FY 1991.

The most recent work in this project has involved the construction and testing of a four-resonance probe with RF channels for ^1H , ^{13}C , ^{15}N , and ^{19}F . In Professor Schaefer's laboratory, it was demonstrated that the four-resonance probe works and that spin echo ^{13}C NMR data dephased by ^{19}F can be obtained. The preliminary data clearly show that carbon fluorine distances up to 15 Å can be measured.

This exciting result offers the possibility of measuring very long range structural parameters using NMR and

^{19}F as a selective probe, which is significant in that ^{19}F is a common element that can be substituted for hydrogen in organic molecules. Thus, it may be possible that labeled organics can be used to study the adsorption of organic molecules on solid surfaces, the interaction of organic molecules with biological systems such as DNA and enzymes, and the use of probe organic molecules to follow chemical reactions that occur in solid matrices. In addition, the ^{19}F RETOR technique may be useful in studying the bonding and structural parameters at the solid/solid interface in composite materials.

One of the first experiments to be conducted in FY 1991 using this new probe will involve direct measurements across the interface boundary of composite inorganic polymeric materials. This experiment should result in unique insights into the variations in composition and structural integrity at solid/solid interfaces and offer a unique insight into the effect of moisture and solvent molecules on the distance and chemical reactivity within these difficult-to-study buried interfaces.

Theory, Modeling, and Simulation

Theory, Modeling, and Simulation

Theoretical and computational molecular science will play a critical role in developing molecular-level descriptions of chemical, physical, and biological processes in natural and contaminated systems. Theory provides the conceptual framework for the analysis and interpretation of experimental data. Modeling and simulation provide quantitative information that may be expensive and difficult or even impossible to obtain in the laboratory.

To model molecular processes in the environment requires a fundamental understanding of molecules and their interactions in isolation (gas phase), in liquids, on surfaces, and at interfaces (condensed media). Research in the Theory, Modeling, and Simulation program involves the development of new theoretical methods and modeling and simulation techniques appropriate for the molecular systems found in the environment as well as the application of state-of-the-art methods to environmentally important molecular problems. The latter program combines efforts devoted to rigorous studies of fundamental molecular processes (diffusion, reaction, solvation, absorption, etc.) in model systems with efforts devoted to the simulation of the complex multiatom, multispecies, and multiphase molecular systems prevalent in the environment.

The Theory, Modeling, and Simulation program consists of three research activities:

- molecular theory and modeling - focusing on understanding elementary molecular processes in both the gas and condensed phases
- materials theory and modeling - extending theoretical models of surfaces and materials to oxide, carbonate, and clay mineral systems
- biomolecular modeling and simulation - developing and applying techniques to model enzymatic and other biochemical processes.

Significant accomplishments in each of these research areas are described in the following three sections.

In the fourth section, the Molecular Science Software activities are presented. The computing demands of the molecular science research programs are already substantial and will grow dramatically over the next few

years as new projects involving molecular systems of increasing size and complexity are undertaken, as new staff are added to the program, and as extensive collaborative research projects are initiated. To provide an optimal response to the computing needs of this effort, the Theory, Modeling, and Simulation program will develop and manage the Molecular Science Computing Facility (MSCF) as part of the Environmental and Molecular Sciences Laboratory (EMSL). The scope and goals of the MSCF was the subject of a workshop held at PNL on February 7-8, 1990.

The MSCF will consist of three laboratories:

- a High-Performance Computing Center to provide production computing capabilities for EMSL users
- an Experimental Computing Laboratory to assess new computer architectures that show promise for molecular computations
- a Graphics and Visualization Laboratory to provide high-performance graphics equipment for analyzing molecular simulations.

To ensure full and efficient utilization of the hardware in the MSCF by all EMSL users, the Molecular Science Software project is an integral part of the MSCF.

1. Molecular Theory and Modeling

B. C. Garrett, G. K. Schenter, R. P. McRae, T. H. Dunning, Jr., and R. A. Kendall^(a)

Molecular Theory and Modeling activities are focused on *ab initio* theoretical studies of molecular processes in isolation, in liquids, on surfaces, and at interfaces and on the modeling of these processes in complex environmental systems. The research objectives of this work are threefold:

(a) C. B. Duke, Xerox Webster Research Center, Webster, New York; C. F. Melius, Sandia National Laboratory, Livermore, California; and D. G. Truhlar, University of Minnesota, Minneapolis, Minnesota, also contributed to this work.

- to apply available *ab initio* techniques to study molecular processes involved in the chemistry of the environment, considering both gas- and condensed-phase processes
- to extend current *ab initio* techniques to treat molecular systems of future interest and to develop new techniques for addressing problems that are computationally intractable at present
- to develop more accurate simulation techniques for describing molecular processes occurring in the complex systems found in the environment.

Present applications include studies of gas-phase reactions important in atmospheric chemistry, studies of condensed-phase reactions important in groundwater and soil chemistry, and studies of intermolecular charge transfer as prototypes of dynamical processes that are strongly influenced by the surrounding solvent. There have been two main thrusts in the research on the dynamics of chemical reactions: 1) studies of the reaction-path Hamiltonian approach in chemical reactions in the gas phase and in solution and 2) studies of solvent effects on dynamical processes in which the solvent is treated in a continuum approximation using the Generalized Langevin Equation (GLE). Cluster approaches are also being used to address questions about the effect of solvation on molecular structure, properties, and reactivity, with an emphasis on the chemistry of anions.

Solvent Effects on the Dynamics of Chemical Reactions

The effect of solvation on chemical reaction rates was first treated by Kramers¹ within a simple reaction-path model modified to include the frictional effects of the solvent. Grote and Hynes² generalized this result to include memory effects in the solvent friction using a GLE to describe the heat bath effects. This model is equivalent to a treatment in which the solute reaction coordinate is linearly coupled to an infinite set of independent harmonic oscillators.³ However, from work with reaction-path Hamiltonians in gas-phase reactions, it is known that reaction-coordinate motion can be strongly affected by nonlinear couplings that result from the curvature of the reaction path.

In this work, the importance of reaction-path curvature on the dynamics of reactions in solution is being investigated. Specifically, we are interested in identifying

the role that global recrossings (i.e., recrossings induced by reaction-path curvature) play in chemical dynamics occurring in the condensed phase.

A dynamical system consisting of a three-atom ($A + BC$) collinear system immersed in a solvent bath was studied. Three reactive systems were considered with increasing reaction-path curvature: $H + H_2$, $C_1 + HC_1$, and $C_3 + HC_3$, where C_1 and C_3 represent masses of 12 and 36, respectively.

For all three systems, the same London-Eyring-Polanyi-Sato (LEPS) potential was chosen for the primary system (the solute degrees of freedom) with barrier heights and Sato parameters characteristic of the $H + H_2$ reaction. Also, for all three systems, the dynamics were modeled using the same GLE with a coordinate-independent friction kernel in the $A + BC$ Cartesian coordinate space taken from Grote and Hynes.⁴

The explicit form for the friction tensor was taken to have the diagonal Gaussian components $\exp(-g^2 t^2)$ and off-diagonal terms that contained a $t^2 \exp(-g^2 t^2)$ dependence. The resulting classical equations of motion were numerically integrated using initial conditions sampled from a canonical distribution at the saddle point corresponding to a bath temperature T . By tracking trajectories initiated at the transition-state surface, the correction to gas-phase transition-state theory due to dynamical recrossing could be calculated.

In Figure 1.1, the reaction rates computed from the exact dynamical calculations are compared with the approximate ones from Grote-Hynes theory. The ratios of these rates with conventional transition-state theory are plotted versus the unitless ratio

$$f/(m_B \omega_s)$$

where f = integrated friction
 m_B = the mass of atom B
 ω_s = the absolute value of the imaginary reactive frequency at the saddle point.

The conventional transition-state theory rate constants are computed for the solute degrees of freedom in the absence of the heat bath. Alternatively, transition-state theory can be applied for the total system (i.e., solute plus heat bath). In this case, the dividing surface is effectively defined by a normal mode analysis of the potential for the total system at the saddle point. The resulting expression for the reaction rate is equivalent

Figure 1.1. Comparison of reaction rate ratios by Grote-Hynes theory (dashed curves) and exact dynamics (solid curves) to conventional transition-state theory for three model three-atom reactions in solution plotted versus the ratio of the scaled solvent friction.

to that given by Grote and Hynes. This method was used to compute the Grote-Hynes results shown in Figure 1.1.

In Figure 1.1, it is seen that global recrossings, those that are present even in the gas phase ($f = 0$), cannot be described by Grote-Hynes theory. In addition, the errors become more significant with increasing reaction-path curvature (larger m_A/m_B). Finally, the global recrossings tend to decrease as the friction increases until the exact dynamical and Grote-Hynes results become comparable at higher frictions. Global recrossing is less at high friction; once a trajectory is sufficiently far from the dividing surface, the solute degrees of freedom lose their energy to the heat bath and have insufficient energy to make it back to the dividing surface.

The exact dynamics were then compared with other approximate theories in an attempt to develop a simpli-

fied description of the dynamics. A reaction-path Hamiltonian description of the solute degrees of freedom (rather than the Cartesian coordinate system) was considered as a first step. The results of these calculations were identical to the exact dynamical ones as long as the full potential energy surface was used. However, when the potentials for motions transverse to the reaction path were treated harmonically, substantial differences were found. The nonlinear components of the interacting gas-phase potential influence the resulting macroscopic recrossing.

The formal relation between the exact description of the dynamics and a reaction-path Hamiltonian approach was examined to investigate the feasibility of incorporating reaction-path curvature in a more approximate saddle point model like the Grote-Hynes model. It was concluded that it may not be possible to include global recrossing in a simplified saddle point model.

Variational Transition-State Theory Calculations of Concerted Hydrogen Atom Tunneling

Hydrogen atom and proton transfer are among the simplest elementary processes that occur in aqueous solutions. The direct participation of solvent molecules may play an important role in these processes; for example, multiple water molecules have been shown to participate in intramolecular hydrogen transfer in organic acids.⁵

In the present work, simple prototypes of concerted hydrogen atom transfer processes have been examined for small hydrogen-bonded water clusters—cyclic trimers and tetramers—and hydrogen-bonded clusters of formaldehyde with one and two water molecules. Rate constants for the rearrangement processes are computed using variational transition-state theory with quantum corrections for tunneling.⁶ The variational transition-state theory calculations directly utilize information about the potential energy surface along the minimum energy path obtained from *ab initio* electronic structure calculations with an empirical bond additivity correction (the BAC-MP4 method).⁷ *Ab initio* methods have been used previously to examine saddle points for concerted proton transfer reaction mechanisms in additions to carbonyl groups.⁸ This work extended these studies to include higher levels of electron correlation and follow the entire reaction pathway in order to apply variational transition-state theory and to treat the tunneling process.

Ab initio electronic structure calculations were performed with the Gaussian 88.⁹ The first step in a calculation is to determine the relevant equilibrium geometries for the reactant and product and the saddle point connecting these two stable points. The geometries of these points were optimized at the Hartree-Fock level with a 6-31G* basis set. The minimum energy path connecting the saddle point with the reactant and product was then computed by following the path of steepest descent in a mass-weighted coordinate system. First and second derivatives along the reaction path are obtained from Hartree-Fock calculations. In the BAC-MP4 method, it is assumed that geometries and frequencies can be obtained to a good approximation from Hartree-Fock calculations. The absolute energy, on the other hand, is computed by full fourth-order Møller-Plesset perturbation theory (MP4-SDTQ) in a contracted 6-31G** atomic orbital basis and corrected for errors due to basis set and higher order correlation effects with a bond additivity correction (the BAC).

Rate constant calculations were carried out using the POLYRATE program.¹⁰ These calculations directly utilize the energy and the first and second derivatives along the minimum energy path. Rate constants were calculated by canonical variational theory (CVT)¹¹ with multidimensional quantum mechanical tunneling effects included by a small-curvature semiclassical adiabatic ground-state (SCSAG) transmission coefficient.¹² The SCSAG method includes the effect of "corner cutting" induced by the reaction-path curvature.

The lowest energy cyclic tetramers of water are nearly planar for the OH bonds forming the ring. The BAC-MP4 method predicts that the cyclic trimer and tetramer are bound by 23.6 and 39.2 kcal/mol, relative to free water molecules. The classical barrier heights (without zero-point energy corrections) for the unimolecular rearrangement process are 29.1 and 25.1 kcal/mol relative to the equilibrium structures of the cyclic n-mers. Thus, a substantial drop occurs in the classical barriers when an additional water molecule directly participates in the reaction process.

The reactant, transition-state, and product structures for the hydrolysis of formaldehyde by two water molecules are shown in Figure 1.2. (The structures for the hydrolysis of formaldehyde by a single water molecule are similar.) Hydrolysis by a single water molecule is lower in energy by 10.2 kcal/mol with a classical barrier height of 41.0 kcal/mol. For hydrolysis by two water molecules, these energies are 7.7 and 20.3 kcal/mol,

a) Reactant Structure

b) Transition-State Structure

c) Product Structure

Figure 1.2. Hydrolysis of formaldehyde by two water molecules.

respectively. The observed drop in classical barrier height with additional water molecules participating in the process is quite dramatic (over 20 kcal/mol).

The rates for the hydrolysis of formaldehyde are shown in Figure 1.3. The rate constants for hydrolysis change dramatically with the addition of water molecules. Compared to the reaction with one water molecule,

Figure 1.3. Rate constants calculated by CVT (dashed curves) and CVT/SCSAG (solid curves) methods for hydrolysis of formaldehyde by one water molecule (lower set of curves) and two water molecules (upper set of curves).

the rates of the reaction with two water molecules are enhanced by 2.1×10^9 at 300K. Tunneling is also important for formaldehyde hydrolysis: the tunneling correction factors are 1.6×10^4 with one water molecule and 2.5 for two water molecules at 300K.

In this work, the direct participation of water molecules in the concerted proton transfer process has been addressed, but the large solvating effect of surrounding water molecules on the stabilization of the transition states has not been considered. For the reactions studied here, the barriers are quite high, ranging from ~ 16 to ~ 40 kcal/mol. As a consequence, the resulting rate constants are quite low and would not be measurable from room temperature to 600K. However, it is instructive to note how these rates vary with the number of participating water molecules in the concerted proton transfer and how the number of participating water molecules affects the importance of tunneling.

In an aqueous environment, the solvation stabilization is expected to be greater for the transition state than for the reactants because of the greater ionic character of the transition state. Using an equation of state with critical parameters scaled from changes in the atomic charge of each hydrogen,¹³ it is estimated that the free

energy of activation for the reaction in Figure 1.2b is lowered by 18.3 kcal/mol. Increasing the polar strength of the solvent is expected to decrease the tunneling contribution to the rate constant but increase the proton transfer rate. Further research on the effects of the solvating medium on the concerted proton transfer reaction within the variational transition-state theory formalism is planned.

Twist-Induced Charge Transfer

Complex molecular systems involve interactions and dynamics that occur over multiple space and time scales. One such system that has been studied in detail is the photo-induced twisting dynamics of molecules in polar solvents. In particular, we have developed a new quantitative microscopic model for the time-dependent fluorescence of dimethylaminobenzonitrile (DMABN) in propanol at low temperature (223K). In nonpolar solvents or in the gas phase, DMABN emits a broad blue fluorescence (B fluorescence) upon photoexcitation. In polar solvents, an additional anomalous fluorescence (A fluorescence) is observed. The time dependence of the resulting A and B fluorescence exhibits a rich multiple time scale structure at low temperatures.

DMABN is the simplest of a class of molecules that exhibit this behavior. A mechanism explaining this behavior was first proposed by Grabowski and Lippert^{14,15} and involved a twisted intramolecular charge transfer (TICT). In this class of molecules, charge transfer is directly coupled to the twisting motion of a donor complex relative to an acceptor complex, leading to large changes in the dipole moment. The resulting charge distribution, in turn, interacts with the surrounding polar solvent (see Figure 1.4). Occurring on a longer time scale, the solvent molecules reorient themselves to align with the molecular dipole field, stabilizing the twisted configuration. This system is complex because it involves intramolecular forces, molecular dipole-solvent polarization field interactions, and direct solvent forces (buffeting and friction) that manifest themselves over a large range of time scales.

A model has been developed that explicitly considers the dynamics of the surrounding solvent dielectric relaxation in addition to the direct twisting motion. Previous models consist of two state kinetic models and single reaction-coordinate Langevin theories.^{1,16}

Figure 1.4. TICT mechanism in DMABN. Ellipsoids represent a polar solvent and μ is the dipole moment of the molecule.

These models can adequately describe the high-temperature behavior in which the dynamics may be described in terms of one or two characteristic time scales. This is not the case at low temperature where many scales of interacting dynamics occur within the fluorescence lifetime of the molecule. In addition, our model is the first to identify microscopic mechanisms with all observed time-dependent features.

In the model, we explicitly incorporate the dynamics of two degrees of freedom, the twist angle θ , and the electric field at the center of the molecule E , which represents a collective solvent coordinate. The dynamical motion of these coordinates was described by a coupled set of GLEs. The solvent response to the evolving time-dependent dipole was represented as a homogeneous, time-dependent dielectric surrounding the molecule. Explicit forms for the gas-phase potential energy surface and the twist-dependent dipole moment were incorporated. Radiative losses were included in terms of a twist-dependent transition probability. The frequency shift of the emitted fluorescence due to

the solvent environment was also taken into account, allowing us to unfold time-dependent fluorescence intensities from population dynamics.

From the analysis, three distinct time scales were identified:

- the initial equilibration of the ground-state geometry on the excited-state potential energy surface (<0.1 ns)
- diffusive barrier crossing (~ 0.5 ns)
- the dielectric relaxation of the solvent (>1 ns).

All of these time scales are identifiable unambiguously in the experimental measurements at low temperatures.

Figures 1.5 and 1.6 show a comparison of calculated and experimental emission intensities for DMABN in propanol at 223K.^{17,18} The experimental results

Figure 1.5. Comparison of calculated and experimental normal or "B" state time-dependent fluorescence. Two time scales exist: a fast component < 0.1 ns and a slower component ~ 0.5 ns.

Figure 1.6. Comparison of calculated and experimental anomalous or "A" state time-dependent fluorescence.

include the instrument response. The fast decay of the B state and the fast buildup of the A state are associated with the initial equilibration. The longer time behavior is associated with diffusive barrier crossing from the B to the A state. Figure 1.7 shows the calculated wavelength-resolved time-dependent spectral shift at long time periods. This behavior is dominated by the solvent dielectric relaxation.

References

1. H. A. Kramers, *Physica (Utrecht)* **7**, 284 (1940).
2. R. F. Grote and J. T. Hynes, *J. Chem. Phys.* **73**, 2715 (1980); **77**, 3736 (1982).
3. R. Zwanzig, *J. Stat. Phys.* **9**, 215 (1973).
4. R. F. Grote and J. T. Hynes, *J. Chem. Phys.* **75**, 2191 (1981).
5. E. Grunwald, C. F. Jumper, and S. Meiboom, *J. Am. Chem. Soc.* **85**, 522 (1963); E. Grunwald and S. Meiboom, *J. Am. Chem. Soc.* **85**, 2047 (1963); E. Grunwald and C. F. Jumper, *J. Am. Chem. Soc.* **85**, 2051 (1963); Z. Luz and S. Meiboom, *J. Am. Chem. Soc.* **85**, 3923 (1963); S. N. Vinogradov and R. H. Linnell, *Hydrogen Bonding*, Van Nostrand Reinhold Co., New York, 1971, p. 217; E. Grunwald and D. Eustace, in *Proton Transfer Reactions*, E. Caldin and V. Gold, eds, Chapman and Hall, London, 1975, p. 103.
6. See, for example, A. D. Isaacson, D. G. Truhlar, S. N. Rai, R. Steckler, G. C. Hancock, B. C. Garrett, and M. J. Redmon, *Computer Phys. Comm.* **47**, 91 (1987) and references therein.
7. See, for example, B. C. Garrett, M. L. Koszykowski, C. F. Melius, and M. Page, *J. Phys. Chem.* **94**, 7096 (1990) and references therein.

Figure 1.7. Calculated long time wavelength-resolved fluorescence for DMABN in propanol at 223K.^{17,18} Behavior is dominated by solvent relaxation.

8. I. H. Williams, G. M. Maggiora, and R. L. Schowen, *J. Am. Chem. Soc.* **102**, 7831 (1980); I. H. Williams, D. Spangler, D. A. Femec, G. M. Maggiora, and R. L. Schowen, *J. Am. Chem. Soc.* **105**, 31 (1983); I. H. Williams, *J. Am. Chem. Soc.* **109**, 6299 (1987).
9. M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Raghavachari, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. Martin, L. R. Kahn, J.J.P. Stewart, E. M. Fluder, S. Topiol, and J. A. Pople, *Gaussian 88*, Gaussian Inc., Pittsburgh, Pennsylvania, 1988.
10. For Version 1.1, see Reference 6; for Version 1.5, see A. D. Isaacson, D. G. Truhlar, S. N. Rai, G. C. Hancock, J. G. Lauderdale, T. N. Truong, T. Joseph, B. C. Garrett, and R. Steckler, *POLYRATE Program Manual*, 1988.
11. B. C. Garrett and D. G. Truhlar, *J. Phys. Chem.* **83**, 1079 (1979); *J. Phys. Chem.* **87**, 4553 (1983).

12. R. T. Skodje, D. G. Truhlar, and B. C. Garrett, *J. Chem. Phys.* **77**, 5955 (1982); *J. Phys. Chem.* **85**, 3019 (1981).
13. C. F. Melius, N. Bergan, and J. E. Shepherd, *Symp. (Int.) Comb. [Proc.]* **1990**, 23.
14. E. Lippert, W. Rettig, V. Bonacic-Koutecky, F. Heisel, and J. A. Miele, *Adv. Chem. Phys.* **68**, 1 (1987).
15. Z. R. Grabowski, K. Rotkiewicz, A. Siemiarz, D. J. Cowley, and W. Baumann, *Nouv. J. Chim.* **3**, 443 (1979).
16. B. Bagchi, *Chem. Phys. Lett.* **135**, 558 (1987).
17. S. G. Su and J. D. Simon, *J. Chem. Phys.* **89**, 908 (1988).
18. F. Heisel and J. A. Miele, *Chem. Phys. Lett.* **100**, 183 (1983).

2. Materials Theory and Modeling

J. P. LaFemina, A. C. Hess, T. J. Godin, A. J. Skinner, G. K. Schenter, and D. L. Lessor^(a)

There is a critical need to understand the geochemical processes controlling the concentration of contaminants in the subsurface so that more accurate models of contaminant flow in the groundwater can be constructed and effective remediation technologies can be developed to remove or immobilize contaminants from the subsurface environment. Unfortunately, little is known about these reactions, their mechanisms, or even the structure of the surfaces on which they occur at the molecular level. This lack of understanding has severely limited the development of the rigorous predictive models needed to forecast contaminant movement in the subsurface. Improved models at the microscopic, macroscopic, and mesoscopic scales can only be derived from a complete understanding of the surfaces and surface contaminant reactions at the atomistic level.

(a) C. B. Duke, Xerox Webster Research Center, Webster, New York; V. R. Saunders, Daresbury Laboratory, Warrington, England; and R. Dovesi, C. Pisani, and C. Roetti, Università di Torino, Torino, Italy, also contributed to this work.

Present research activities in Materials Theory and Modeling seek to obtain a detailed microscopic understanding of the surface structure and chemistry of mineral oxides and compound semiconductors. These materials are important in areas as diverse as the transport of groundwater contaminants, the creation of advanced electronic and optoelectronic devices, and the production of advanced materials.

Theory of the Electronic and Atomic Structures of Insulator Surfaces

The sections below describe work conducted on the following topics: the surface structure of insulators, the structure of adsorbates on surfaces, the calculation of surface phonon frequency distributions, and the low-energy electron diffraction (LEED) and low-energy positron diffraction (LEPD) from insulator surfaces.

Surface Structure of Insulators

A comprehensive model has been formulated to describe surface atomic geometries, chemical bonding, and electronic structure of the cleavage faces of tetrahedrally coordinated compound semiconductors. This model includes both the zincblende and wurtzite structures. The most significant result to emerge from these studies is the existence of a universal relaxation for each of the cleavage faces of III-V and II-VI materials in both the zincblende and wurtzite crystal structures, despite their vastly different bulk and small molecule chemistries. These relaxations proceed via bond-length-conserving rotations of the surface atoms, are driven by the surface state lowering that accompanies the redistribution of the surface dangling-bond charge density, and are primarily a function of the surface topology.

This model has now been extended to include cubic (MgO), cristobalite (SiO_2), and tridymite (SiO_2) oxides.¹ These studies have demonstrated that, as with the tetrahedrally coordinated compound semiconductors, the topology of the surface is the paramount factor determining the nature of surface atomic relaxation. Surfaces with the ability to undergo approximate bond-length-conserving relaxations (for example, SiO_2) will exhibit large atomic surface relaxations while those whose topology precludes such motion (for example, MgO) will exhibit very small relaxations.

In addition to the usual dangling-bond to back-bonding driving force for surface relaxation, an additional driv-

ing force was identified, namely, a lowering produced by the rehybridization of O nonbonding p orbitals. However, the effect of surface topology seems predominant because for MgO(001) significant rehybridization is precluded by the surface topology, while in the SiO_2 allotropes large bond-length-conserving relaxations are topologically allowed and energetically favored by a suitable surface-state lowering mechanism. Hence, the surface structural chemistry of oxide cleavage surfaces reflects the interplay of both surface topology (via the ability to undergo bond-length-conserving relaxations) and local chemical bonding (via the participation of p electrons in bonding versus nonbonding surface-state bands).

Figure 2.1 shows the ideal and relaxed β -cristobalite SiO_2 (110) surface. The surface relaxes via bond-length-conserving motions of the cations (Si) towards the bulk and the anions (O) out from the surface.

The dispersion of the surface-bound states is shown in Figure 2.2. The stabilization of the surface state $S_6(p^3)$ provides the primary driving force for the reconstruction. The orbital nature of this state involves the back bonding of the rehybridized top-layer O p_z -dominated p_3 orbital with the top-layer Si (now rotated towards the bulk) and second-layer O (now rotated toward the surface) p_x -dominated p_3 hybrid.

Structure of Adsorbates on Surfaces

The adsorption of an ordered $p(1 \times 1)$ monolayer of Sb on the (110) surface of the III-V compounds reverses the surface relaxation, with the adatoms occupying both cation and anion positions in the surface layer. Using a tight-binding total-energy formalism previously developed for these systems, two new minimum-energy surface structures were identified for $p(1 \times 1)$ overlayers of Sb on the (110) surface of III-V compound semiconductors^{2,3} (see Figure 2.3). The first is the "epitaxial on top structure" (EOTS) in which Sb zigzag chains are commensurate with, and on top of, the Ga-As unreconstructed surface zigzag chains.

This structure differs from the previously found "epitaxial continued layer structure" (ECLS) by virtue of the registry of the Sb chains "on top of" rather than "in between" the substrate Ga-As chains. Like the ECLS, the EOTS is compatible with both scanning tunneling microscopy (STM) and photoemission data.

The second new structure is the "epitaxial overlapping chain structure" (EOCS), where the Sb chains are 180°

○ Si ● O a) Ideal (truncated bulk) surface

○ Si ● O b) Fully relaxed surface

Figure 2.1. Schematic indication of the β -cristobalite $\text{SiO}_2(110)$ surface. The surface relaxes via approximately bond-length-conserving motions of the cations (Si) towards the bulk and the anions (O) out from the surface.

Figure 2.2. Energy dispersion of surface-bound states for β -cristobalite $\text{SiO}_2(110)$. Surface states are denoted by $S_n(i)$, while second-layer derived states are denoted by $A_n(i)$ (anion derived) and $C_n(i)$ (cation derived). All are indicated by a dashed line. The label (i) indicates the hybridization of the surface state. The inset shows the (110) surface Brillouin zone. The bold dot-dashed lines show the position of surface state $S_6(p^3)$ before relaxation while the bold dashed line indicates its position after relaxation. The shaded area indicates the projection of the bulk bands.

out-of-phase with, and on top of, the Ga-As substrate chains. This structure is, however, incompatible with both LEED and STM data for $\text{GaAs}(110)\text{-p}(1\times 1)\text{-Sb}$.

In summary, by utilizing chemically distinct starting structures in total-energy minimization calculations, two new possible minimum-energy surface atomic

structures for $\text{p}(1\times 1)$ overlayers of Column V elements on the (110) face of III-V compound semiconductors were identified.^{2,3} Moreover, the EOTS is compatible with current STM and photoemissions data, thereby rendering it a viable potential alternative to the previously determined ECLS to be checked by analysis of LEED intensity data (see following section). Finally, simple geometric considerations suggest that $\text{Bi/GaP}(110)$ and $\text{Bi/GaAs}(110)$ may also exhibit the EOTS; and computations on these systems are in progress.

Calculation of Surface Phonon Frequency Distributions

The discovery of surface rotational phonons on $\text{GaAs}(110)$ via helium atom diffraction and their interpretation via tight-binding total energy (TBTE) and bond-charge dynamical models has stimulated interest in dynamical strains at semiconductor surfaces. Since Sb and Bi form epitaxial $\text{p}(1\times 1)$ overlayers on $\text{GaAs}(110)$ and other III-V(110) surfaces, the calculation and observation of the modification of the surface and interface vibrational normal modes by these overlayers offers the opportunity to determine quantitatively the dynamical strain fields at semiconductor interfaces.

To determine the experimental conditions needed to observe these modes, we have extended the total-energy models for $\text{GaAs}(110)\text{-p}(1\times 1)\text{-Sb}(1\text{ML})$ to calculate the dynamical force fields and normal mode spectra of the Sb overlayer, as well as the rotational normal mode spectra of an incompressible system. The character of these modes revealed the profound effects of the adsorbed Sb on the clean $\text{GaAs}(110)$ normal modes, as well as set the range of energies and polarizations to be examined by helium atom diffraction and high-resolution energy loss spectroscopy in order to observe the surface phonon spectra of $\text{GaAs}(110)\text{-p}(1\times 1)\text{-Sb}(1\text{ML})$.

The discovery and characterization of this new branch of rotational surface phonons has led us to consider the question of surface phonons in general. The increased use of quantum-mechanical molecular dynamics (QMMD) simulations to determine the atomic, electronic, and vibrational properties of solids has recently been spurred by the development of an efficient method for determining atomic forces directly from a first-principles local-density functional-molecular dynamics simulation by Car and Parrinello.⁴ One advantage to the use of QMMD simulations over

Figure 2.3. Different surface atomic structures for GaAs(110)-p(1x1)-Sb(1ML) system.

conventional quantum-mechanical computations of total-energy derivative properties is the ability of MD simulations to investigate temperature effects.

Using the TBTE models that have been successfully used to characterize the atomic and electronic structures of these systems, QMMD simulations were performed to determine both the bulk and (110) surface phonon frequency distributions for GaP, GaAs, GaSb, InP, InAs, and InSb. Our approach utilizes the TBTE model to compute the Hellman-Feynman forces used

to drive the MD simulation. A method for computing bulk phonon dispersion curves has been developed, and the dependence of both bulk and surface phonon frequencies upon temperature has been explored.

Low-Energy Electron and Positron Diffraction from Insulator Surfaces

LEED and LEPD intensity analyses are important tools in determining the surface atomic structure and the mechanisms of surface relaxation. A combined

experimental and theoretical LEPD program carried out with researchers at Brandeis University and Xerox Webster Research Center has examined the Cu(111) surface in an attempt to characterize the importance of surface loss processes at large angles of incidence.⁵ The results suggest that at these angles ($\theta \geq 30^\circ$), and at electron energies greater than 50 eV, surface loss mechanisms such as plasmon and/or positronium formation are minimal, and the usual dynamical multiple scattering methodology is appropriate. However, at lower electron energies, strong resonances occur associated with both the multiple elastic scattering phenomena within atomic layers of copper parallel to the surface and with the onset of new inelastic channels (for example, plasmon creation).

An examination of the differences between LEED and LEPD and the influence of the ion-core potential in determining these differences has revealed that the attractive electron-ion-core potential results in material-sensitive phase shifts while the repulsive positron-ion-core potential results in material-insensitive phase shifts.⁶ This fact seems to account for most of the differences between LEED and LEPD.

As described in the above section, TBTE computations have identified an alternative structure (EOTS) (see Figure 2.3) for the GaAs(110)-p(1x1)-Sb system. Bismuth, like Sb, also forms epitaxial monolayers on GaAs(110), and a previous LEED analysis had suggested that its atomic structure was similar to the ECLS. This computation, however, did not consider the EOTS. Consequently, a comprehensive multiple-scattering analysis of the LEED intensities from Bi/GaAs(110), Sb/GaAs(110), and GaAs(110) was performed in collaboration with the Montana State University Advanced Materials Center.⁷⁻⁹

Using an LEED analysis technique extended to include a multidimensional optimization procedure, the EOTS failed to provide an acceptable fit for either the Sb or Bi overlayer systems. Consequently, we have established that the bonding of Bi on GaAs(110) should be identical to that of Sb and that the most probable structure is the ECLS.

The application of LEED to the study of insulator surfaces is complicated by surface charging effects. Modulated beam techniques can be used to reduce these effects, and we conducted a modulated beam LEED study on MgO(001).¹⁰

In addition, a dynamical LEED intensity analysis was performed using two models to describe the electron attenuation: a constant imaginary potential model and the attenuation model of Tanuma, Powell, and Penn¹¹ based on a modified Bethe equation. It was found that both models gave approximately the same agreement with experimental results. The geometric parameters determined via the LEED structural analysis (a surface rumple of $2 \pm 2\%$ of an interlayer spacing and a contraction of the first interlayer spacing of $0 \pm 1\%$) are in quantitative agreement with the results of previous LEED and reflection high-energy electron diffraction (RHEED) studies as well as with the results of TBTE computations,¹ *ab initio* Hartree-Fock computations, and the results of shell model studies.

***Ab Initio* Solid-State Quantum Chemistry Studies of Hydrous Phyllosilicates**

The following sections describe work conducted on the electronic structures of kaolinite and sodalite.

Electronic Structure of Kaolinite

Clay minerals are the most common decomposition products of aluminosilicates that have been subjected to aqueous environments under earth-surface conditions. Since it has been estimated that over 83% of the earth's continental crust is composed of oxygen, silicon, and aluminum (the basic components of aluminosilicates),¹² it is not surprising that clay minerals are the major components of both sediment and sedimentary rocks. These hydrous aluminosilicates are typified by very small grain sizes (commonly 2 to 10 μm), leading to large surface areas and sheet-like structures, which causes the material to function as a natural ion-exchange media.

It is therefore believed that these minerals play a central role in both chemical reactivity and complex geochemical processes such as subsurface transport of hazardous materials. The goal of this research is to gain a fundamental understanding of both the mineral chemistry and physics of these materials using techniques established in *ab initio* computational solid-state quantum chemistry.

The computational techniques currently being used to accomplish the above goal are based on self-consistent field (SCF) solutions of the Hartree-Fock-Roothan equations subject to periodic boundary conditions. This approach is a multistep process that begins by constructing the direct space Fock matrix. The resulting Fock matrix and the associated overlap matrix are then Fourier transformed to reciprocal space where the one-electron eigenvalue equations take on a block diagonal form that can then be solved to yield the crystal orbitals (linear combinations of Bloch functions). These eigenvectors can then be used to obtain a new density matrix that is used to construct a new direct space Fock equation and the entire procedure is repeated until the total energy converges. This method has been fully implemented in the *ab initio* program CRYSTAL.¹³

The explicit evaluation of the exchange energy performed in this procedure contrasts with more standard solid-state techniques that typically use local density approximations to treat the contributions of both exchange and correlation energies to the Fock operator. It is also important to note that this method draws heavily upon established concepts and technologies in molecular quantum chemistry. For example, the close correspondence of such essential components as basis sets, integral evaluation routines, and SCF iteration schemes between the molecular and crystalline environments allows significant portions of molecular-based technical experience to be transferred directly to the periodic condensed-phase systems.

The primary advantage of the method over the evaluation of large molecular clusters for systems possessing periodicity is that the full crystallographic space group symmetry can be exploited. This both eliminates "edge" effects associated with using boundary conditions not representative of those found in the crystalline environment and reduces the amount of effort expended to the minimum amount.

These methods were recently used to investigate the properties of kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. The bulk band structure, total and projected density of states, electrostatic charge densities, and electrostatic potentials were evaluated using both minimal and split valence basis sets. To the best of our knowledge, these calculations represent the first *ab initio* study of the properties of a clay mineral. All calculations were carried out for a standard 17-atom P_1 model of the reduced C_1 unit cell obtained by Bish and Von Dreele¹⁴ from x-ray diffraction. Since the positions of the hydrogen

atoms in the structure and consequently the bravais lattice in kaolinite are currently a subject of debate,¹⁵ we placed the hydrogens in the plane of the O-Al-O-Al rings.

The resulting crystal structure is shown in Figure 2.4; it can be seen to be composed of sheets of corner-sharing SiO_4 tetrahedra linked to edge-sharing AlO_6 octahedra by common oxygen atoms stacked parallel to the c-axis. Additionally, two types of hydrogen atoms can be found in the structure: 1) those associated with oxygen atoms in the close-packed layer above the aluminum layer and extending into the interlayer region (known as outer hydrogens) and 2) those bonded to oxygen atoms in the close-packed layer below the aluminum layer that extend into the intralayer cavity toward the silicate rings (known as inner hydrogens).

It has been proposed¹⁶ that the center of the silicate rings, known as the ditrigonal cavity, is capable of functioning as a weak lewis base and therefore

Figure 2.4. Kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ P_1 symmetry.

demonstrates some degree of chemical reactivity (see Figure 2.4). To test this assertion and to investigate the forces experienced by a positively charged particle positioned in the interlayer region of the structure, we evaluated both the electrostatic potential and the charge density along a reaction coordinate parallel to the c-axis and penetrating the center of the ditrigonal cavity.

Figure 2.5 shows computed electrostatic potentials for a region of the structure whose x and y coordinates are outlined in Figure 2.4 and whose z-coordinates range from the center of the interlayer space ($z = -1.60$ bohr) to a position 0.57 bohr from the oxygen plane. As these computations were carried out using a positive test charge, positive regions in the structure are depicted as high points on the surface and regions of negative electrostatic potential are depicted as depressions. For example, by comparing the illustration of the structure in Figure 2.4 with the potential plot shown in Figure 2.5 at $z = -1.03$ bohr, the positions of the various atoms and their contributions to the potential can be seen.

For a value of $z = -1.60$ bohr, it can be seen that the electrostatic potential experienced by a positive test charge placed in the center of the layer space consists predominantly of negative regions centered on the oxygen atoms of the silicate rings and a slightly negative region in the center of the ditrigonal ring (right side of figure in center). The fact that the center of the ditrigonal cavity possesses only a slightly negative electrostatic potential indicates that bulk kaolinite should have little tendency to incorporate positively charged species into this region of the structure.

The results discussed above for kaolinite were computed for a material that possessed periodicity in three dimensions. Calculations are now underway to evaluate the properties of kaolinite surfaces to determine if cleaving the structure introduces any electronic surface states that could account for charge buildup in the silicate ring network.

Electronic Structure of Sodalite

Periodic *ab initio* HF-LCAO calculations for the zeolite sodalite $\text{Al}_6\text{Si}_6\text{Na}_6\text{O}_{24}\text{C}_{12}$ were recently completed. This material represents one of the larger computations carried out to date; the unit cell contains 318 atomic orbitals and some 476 electrons. The bulk

a) $Z = -1.03$ bohr

b) $Z = -1.32$ bohr

c) $Z = -1.60$ bohr

Figure 2.5. Silicate ring electrostatic potential (kaolinite).

band structure, total and projected density of states, and electrostatic potential maps of the interior cavities of the structure have been evaluated. Future studies of sodalite will center on investigating the effect that various atom centers have on electrostatic cavity potentials.

References

1. J. P. LaFemina and C. B. Duke, "Dependence of Oxide Cleavage Surface Structure on Crystal Structure and Local Chemical Bonding," *J. Vac. Sci. Tech.* (in press).
2. J. P. LaFemina, C. B. Duke, and C. Mailhot, "New Surface Structures for Column V Overlayers on the (110) Surface of III-V Compound Semiconductors," *J. Vac. Sci. Tech.* B8, 888 (1990).
3. J. P. LaFemina, C. B. Duke, and C. Mailhot, "New Surface Atomic Structures for III-V(110)-p(1x1)-Sb(1ML): Chemical Bonding and Electronic Structure," in *Atomic Scale Calculations of Structure in Materials*, M. A. Schluter and M. S. Daw, eds., Materials Research Society, Pittsburgh, 1990, pp. 41-46.
4. R. Car and M. Parrinello, *Phys. Rev. Lett.* 55, 2471 (1985); 60, 204 (1988).
5. D. L. Lessor, C. B. Duke, K. F. Canter, P. H. Lippel, G. R. Brandes, T. N. Horsky, and A. P. Mills, "Low-Energy Positron Diffraction on Cu(111)," *J. Vac. Sci. Tech.* (in press).
6. D. L. Lessor and C. B. Duke, "Analysis of the Differences Between Low-Energy Electron and Positron Diffraction: The Ion Core Potential," *Surf. Sci.* 225, 81 (1990).
7. W. K. Ford, T. Guo, D. L. Lessor, and C. B. Duke, "Dynamical LEED Analysis of Bi and Sb Epitaxy on GaAs(110)," *Phys. Rev. B* (in press).
8. W. K. Ford, T. Guo, S. L. Lantz, K. Wan, S.-L. Chang, C. B. Duke, and D. L. Lessor, "Bi and Sb Adsorption on III-V(110) Substrates: Growth, Order and Structure," *J. Vac. Sci. Tech.* B8, 940 (1990).
9. C. B. Duke, D. L. Lessor, T. Guo, and W. K. Ford, "Low-Energy Electron Diffraction Intensity Analysis of the Atomic Geometry of p(1x1) Monolayers of Bismuth on GaAs(110)," *J. Vac. Sci. Tech.* A8, 3412 (1990).
10. D. L. Blanchard, D. L. Lessor, J. P. LaFemina, D. R. Baer, W. K. Ford, and T. Guo, "A LEED Study of the MgO(100) Surface Structure," *J. Vac. Sci. Tech.* (in press).
11. S. Tanuma, C. J. Powell, and D. R. Penn, *J. Vac. Sci. Tech.* A8, 2213 (1990).
12. B. Mason and C. B. Moore, *Principles of Geochemistry*, John Wiley and Sons, New York, 1982, 4th ed., p. 49.
13. R. Dovesi, C. Pisani, C. Roetti, and V. R. Saunders, *Program Crystal*, Quantum Chemistry Program Exchange, Program #577, Indiana University, Department of Chemistry.
14. D. L. Bish and R. B. Von Dreele, *Clays and Clay Minerals* 37, 289 (1989).
15. R. F. Geise, Jr., "Hydrous Phyllosilicates," *Reviews in Mineralogy*, Vol. 19, S. W. Bailey, ed., Mineralogical Society of America, Washington, D.C., 1988.
16. G. Sposito, *The Surface Chemistry of Soils*, Oxford University Press, New York, 1984.

3. Biomolecular Modeling and Simulation

R. L. Ornstein, M. D. Paulsen,^(a) M. B. Bass,^(a) G. E. Arnold,^(a) B. J. Lewis,^(b) G. A. Sanders,^(c) J. M. Smolen,^(c) S. L. van Wagoner,^(c) W. A. Jaquysh,^(c) and J. A. Braatz^(c)

X-ray crystallography and spectroscopic techniques are yielding invaluable three-dimensional structural

(a) NORCUS postdoctoral fellow.

(b) Visiting summer professor, Elizabeth City State University, Elizabeth, North Carolina.

(c) NORCUS predoctoral intern.

information about biomolecules. Modeling and simulation of complex biomolecular systems, using both classical and quantum techniques, can provide detailed information on the structure and dynamics of proteins and enzymes.

The primary activity in the present Biomolecular Modeling and Simulation program is to develop and apply molecular modeling and simulation methods to study the structure/function/dynamic relationships of biodegradative enzymes and to design natural and artificial enzymes with a capacity for improving remediation of hazardous and recalcitrant substances at DOE sites. A secondary purpose of this program is to develop and apply molecular simulation methods to better understand a variety of structure/function/dynamic relationships of proteins and nucleic acids that impact other important human health and environmental issues.

Molecular Simulations on Enzymes

The following sections describe work conducted on the following topics: the structure/function relationship for biodegradative enzymes, the homologous mapping of cytochrome P450, and redesigning enzymes.

Structure/Function Relationships for Biodegradative Enzymes

Only a few important microbial biodegradative enzymes have had their three-dimensional structures solved by experimental methods. In the absence of such structural information, it is not currently possible to gain an understanding of basic structure/function/dynamic relationships or to use rational engineering methods to redesign an enzyme for enhanced biodegradative functions. Nevertheless, protein structures determined by x-ray crystallography or solution nuclear magnetic resonance (NMR) methods generally suffer from the following limitations:

- The structural image is an average in time and space.
- Conformational details are usually unrecoverable for structures less than 5% to 10% in population.
- Molecular surface properties are often significantly deformed due to crystal lattice packing in the solid state or due to solution differences from those in

in vivo conditions, such as when the pH is significantly lowered or raised or when various agents are added to reduce precipitation at high protein concentrations.

- Simulations may be inherently better suited to uncover the location and dynamic nature of access channels connecting an enzyme's molecular surface with a buried active site.

Currently available theoretical simulation methods, starting from a high-resolution experimental structure, can potentially help resolve these issues, as well as lead to a better understanding of the dynamic mobilities and fluctuations inherent in enzyme structure and function.

Cytochromes P450 are a superfamily of monooxygenase proteins present in all the kingdoms of living organisms. The active center of the P450 is the iron protoporphyrin moiety. Although this enzyme family is best known for its mixed-function oxidation reactions, cytochromes P450 are involved in numerous categories of oxidation and reduction.¹ A wide range of alkane and aromatic compounds, including environmental toxins and chemical carcinogens, are hydroxylated by P450 in mammals; this enzyme class "may catalyze the widest variety of reactions of any known enzyme."² Cytochromes P450 of microorganisms may be even more diverse than in eukaryotes.³

During the last year, we performed several molecular dynamics simulations on the biodegradative enzyme cytochrome P450cam.⁴⁻⁷ This enzyme contains over 400 amino acids (over 7000 atoms are involved in the simulations after hydrogens, heme, substrate, and waters of crystallization are added).

Figure 3.1 depicts the results from a 175-ps simulation at 300K, with camphor bound at the active site in P450cam using the BIOSYM, Inc. program DISCOVER on the Hanford CRAY X-MP. The plausibility of the present simulation can be judged by the overall integrity of the enzyme.

The root mean square (rms) deviation from the starting x-ray coordinates for all main chain atoms over the last 125 ps of the simulation is about 1.6 Å (Figure 3.1a), while the radius of gyration is also very stable and close to the starting value (Figure 3.1a). The separation distance between the keto oxygen of camphor and the hydroxyl oxygen of Tyr 96, which

a) Time course variation of the rms deviation for all main chain heavy atoms between the x-ray coordinates and the simulated ones (thin line) and time course variation of the radius of gyration (thick line).

b) Time course variation in the separation distance between the keto oxygen of camphor and the hydroxyl oxygen of Tyr 96 (thick line) and variation of the distance between the heme iron and the center of mass of camphor (thin line).

Figure 3.1. Analysis of 175-ps molecular dynamics simulation on camphor-bound cytochrome P450cam.

c) Comparison of the rms fluctuations between experimental (upper curve) and simulated (lower curve) values for residues 200 to 414.

Figure 3.1. (contd)

forms a hydrogen bond based on the x-ray structure, is maintained at the hydrogen-bonded separation distance throughout the simulation except for short excursions (Figure 3.1b). In addition, the distance between the heme iron and the center of mass of camphor undergoes only modest fluctuations (Figure 3.1b).

The experimental and simulated rms fluctuations in atomic position of the heavy atoms averaged per residue, plotted as a function of residue number (for residues 200 to 414), are compared in Figure 3.1c. Although the curves exhibit an expected baseline separation, the peaks and valleys are strongly correlated. Taken together, the above data indicate that the average properties observed in the simulation are indeed consistent with the average properties reported in the crystal structure determination. This implies that details from the present simulation that may not be resolvable from the experimental data may indeed be trustworthy. A cautionary note is, however, appropriate. Neither the crystal nor the simulation will be too trustworthy with respect to the details of structure and motion of the surface-exposed residues. This is understandable since the molecular surface is prone to lattice-packing forces. If bulk solvent effects were

adequately incorporated, the simulated result may produce more accurate details about the molecular surface.

We have analyzed the detailed dynamic motion of each amino acid residue that lines the buried active site in P450cam from the 175-ps simulation. Most of the backbone and sidechain atoms of the active site residues are very stable as is the case for the chi-2 dihedral angle of Tyr 96 (Figure 3.2a), but surprisingly chi-2 of Phe 87 exhibits very significant flexibility (Figure 3.2a).

"One puzzling question regarding substrate binding is how the camphor molecule gains access to the active site. Unlike many enzymes, the active site of P450cam does not define an open cleft at the molecular surface but is well-sequestered with no obvious route to the pocket."⁸ Thus, significant dynamic fluctuations of the enzyme are required in order for camphor to bind and for the product to exit. Molecular dynamics simulations are the method of choice for gaining a solid understanding of these mechanistically critical pathways. We have initiated simulations focused on gaining a better understanding of this process. Achieving this level of understanding is essential to our planned

a) Time course variation of Tyr 96 (thick line) and Phe 87 (thin line) chi-2 sidechain dihedral angle from a 175-ps molecular dynamics simulation.

b) Stereoview of active site and residues adjacent to the path of camphor during an "activated" simulation with an external force pulling the substrate out of the pocket. The pathway taken by the camphor is indicated by the thick line that connects the center of mass in successive structures saved during the simulation at regular time intervals.

Figure 3.2. Analysis of active site properties for cytochrome P450cam.

design studies that will attempt to optimize structural pathways for the entry and exit of targeted pollutants (see below). As indicated by the data in Figure 3.2, camphor is very stable in the active site of P450cam during a 175-ps simulation.

We believe that the entry/exit process takes tens to hundreds of microseconds; therefore, standard dynamics simulations are not currently expected to uncover the details of this process. Thus, the use of a variety of "activated" simulation methods is being explored, where external forces are gently applied and/or the temperature of the simulation is raised.

Figure 3.2b shows the results of one such activated simulation in which external forces were used; the active site residues and residues along the pathway are shown in the stereoview and the center of mass of the camphor molecule is traced by the thick solid line. This is one of several pathways found to date. It is interesting to note that Phe 87 appears to play a critical "switching" role in this pathway and that it has a very flexible (and bulky) sidechain (Figure 3.2a). Much more analysis remains to be done, however, before the possible pathways can be ranked and the underlying interactions and dynamics can be described.

Homologous Mapping of Cytochromes P450: How Nature Designs the Active Site

Due to the difficulty in handling the vertebrate protein, much of what is known about the details of the cytochrome P450 structure and function stems from studies with cytochrome P450cam obtained from the soil bacteria *Pseudomonas putida*. The phylogenetic and secondary structure relationships of vertebrate P450 sequences and P450cam were recently analyzed.⁹ It is therefore of considerable interest to map and generate three-dimensional structures of P450s with different substrate specificities in order to uncover how nature redesigns the active site of P450s for different substrate specificities.

During the last year, we began to pursue methods of sequence alignment for achieving optimal alignments between P450cam and cytochromes P450 with specificities for substrates similar to targeted pollutants. Doing so is important because the active site residues are found in several disjoint regions of the sequence. Assuming that secondary structural domains are preserved from one sequence to another, we used the principle that the alignment that produces the fewest destructive inserts or deletions has the greatest proba-

bility of being correct. Molecular dynamics simulations will then be performed to obtain reasonable three-dimensional structures. We plan to assess the level of specificity observed in the modeled cytochromes P450 for their native substrates versus that for the "wrong" substrate. This later marker will give a good measure of success or failure. Once we can achieve these goals, these principles can be extrapolated to better design P450cam mutants specific for key recalcitrant pollutants such as certain halogenated hydrocarbon solvents.

Redesigning Enzymes to Enhance Environmental Remediation

Hazardous substances derived from the waste products of energy production, national defense, and industrial activities have entered the environment through routine disposal practices and accidents. In some cases, synthetic or foreign substances may be readily decomposed by natural microorganisms due to coincidental metabolism or due to fortuitous evolution of new enzymatic pathways. However, other substances may be of considerable concern for a variety of reasons.

First, extant catabolic pathways in microorganisms able to degrade these compounds may have low throughput so that timely removal of compounds is not adequate from an environmental or human health perspective. Second, some compounds may be extremely recalcitrant and their degradation may require extensive evolution of one or many enzymes. Although microorganisms have the capacity to evolve to enzymes able to attack most chemical groups, the evolution of modified catabolic pathways will proceed very slowly if multiple genetic changes are simultaneously required for enzyme adaptation. Since each mutation is by itself a rare event, a basic premise of our research is that "designing" multiple changes into an enzyme is more efficient than waiting for them to occur biologically either through natural selection or under laboratory-controlled conditions.

The objectives of this research are to 1) improve and expand the degradative capacity of biodegradative enzymes in indigenous microorganisms and 2) design artificial enzymes for extracellular degradation in harsh environments where microorganisms may be unable to grow at adequate levels. Efforts will focus on developing systems for remediation of DOE site contaminants and important regional contaminants such as dioxanes. Due to the complexity and interdisciplinary nature of our objectives, close collaborations with scientists in the PNL's Environmental Science Research Center and

several universities have been established. These collaborations play a decisive role in our fundamental and applied enzyme redesign studies.

In order to successfully carry out a rational design study to alter an enzyme's specificity, it is necessary to have adequate structural data about an enzyme, its active site, its interactions with the substrate, and an understanding of its mechanisms of action. Such information is currently available only for the P450cam variant of the ubiquitous biodegrading and detoxifying superfamily of enzymes known as cytochromes P450.¹⁰

We are currently using available experimental data, information from homologous mapping studies, and recent P450cam simulation data coupled with modeling studies to deduce "mutant" enzymes with optimal specificity and catalytic efficiency for alternate substrates.

We are testing our ability to institute mutations that demonstrate control over each of the following decoupled components: the active site, the access channels, and the recognition sites on the molecular surface.

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. P450cam catalyzes the hydroxylation of camphor to yield 5-exo-hydroxycamphor; but norcamphor, unlike the natural substrate camphor, yields three different products:¹¹

- 5-exo-hydroxynorcamphor (45%)
- 6-exo-hydroxynorcamphor (47%)
- 3-exo-hydroxynorcamphor (8%) (Figure 3.3).

Figure 3.3. Cytochrome P450cam substrates camphor and norcamphor and their resulting hydroxylated product specificities.

X-ray crystallography has shown that norcamphor binds to the active site in the same position as camphor (that is, with the 5-position carbon of the substrate being the closest heavy atom to the heme iron). While this explains why the 5-position is the preferred hydroxylation site, the x-ray data offer no insight into the mechanism for hydroxylation of the 3-position.

To test our ability to specifically redesign the active site of P450cam and to attempt to explain how the 3-position of norcamphor can serve as a hydroxylation position, a 200-ps simulation on the norcamphor-bound P450cam complex was conducted.¹²⁻¹³ The rms deviation of the simulated coordinates from the x-ray crystal (provided by Professor T. L. Poulos, University of Maryland) starting positions for all heavy atoms (backbone and sidechains), all main chain atoms, and all secondary structure (alpha helical and beta strand) main chain atoms are shown in Figure 3.4. It is apparent that the integrity of the enzyme is maintained throughout the simulation, whereas the average rms deviation during the last 150 ps of the simulation is

only 1.1 Å and 1.6 Å for the secondary structure domain main chain and all main chain atoms, respectively.

Figure 3.5a depicts the variation over the simulation for the distance between the heme iron and the 3- and 5-position carbons of norcamphor. Interestingly, after the equilibration phase (the first 50 ps), the 3-position carbon of norcamphor is about as close to the heme iron as the 5-position carbon in roughly 25% of the structures. The closest approach of the 3-position carbon of norcamphor to the heme occurs at about 95 ps into the simulation. This conformation is shown in the lower right of Figure 3.5b, while the x-ray orientation is shown in the lower left of Figure 3.5b.

On one hand, the data in Figure 3.5 show that norcamphor has sufficient rotational mobility in the active site to account for the observed hydroxylation preferences. Therefore, it is not necessary for substrate to enter this deeply buried active site prealigned for catalytic activity. We have found that camphor has a

Figure 3.4. Time course variation of rms deviations resulting from a 200-ps simulation of norcamphor-bound P450cam. The deviation between the x-ray coordinates and simulated values are shown for all heavy atoms (top line), all main chain atoms (middle line), and only secondary structure domain main chain atoms (bottom line).

a) Time course variation for the distances between the heme iron and norcamphor 5- and 3-position carbons indicated by the thin and thick solid curves, respectively.

b) Active site geometry from the x-ray crystal structure (lower left) and at 95 ps into the simulation (lower right) are given.

Figure 3.5. Active site mobility of norcamphor during a 200-ps molecular dynamics simulation. Note the large orientational shift in norcamphor.

significantly reduced level of rotational mobility in the active site in comparison to norcamphor. On the other hand, the data in Figure 3.5 are being analyzed for the presence of correlated dynamic motions with the active site residues to determine the critical "switches" controlling the rotational motion of substrate.

From this vantage point, we are currently attempting to design mutants of P450cam that will preferentially hydroxylate the 3-position of norcamphor and camphor, therefore demonstrating the ability to control active site specificity. Clearly, as noted above, the problems of access channel control and recognition at the molecular surface must then also be addressed. Achieving these intermediate redesign goals will further the goal of modifying the specificity of P450cam to initiate the degradation pathway for targeted pollutants. Plans then call for simulations on deduced mutants and comparisons of structure and dynamic properties observed for the mutant and wild enzymes in order to suggest the most likely candidate sequences for site-directed mutagenesis, cloning, expression, and enzyme activity testing. If *in vitro* activities prove adequate, a series of experiments will be performed to test for activity under a variety of laboratory-simulated environmental conditions.

References

1. F. P. Guengerich and T. L. MacDonald, "Chemical Mechanisms of Catalysis by Cytochrome P450: A Unified View," *Accts. Chem. Res.* 17:9-16 (1984).
2. C. Walsh, in *Enzymatic Reaction Mechanisms*, Chapter 15, W. H. Freeman, San Francisco, 1979.
3. S. G. Sligar and R. I. Murray, "Cytochrome P-450cam and Other Bacterial P-450 Enzymes." In *Cytochrome P-450: Structure, Mechanism, and Biochemistry*, Ortiz, de Montellano, P., ed., Plenum, New York, 1986, pp. 429-503.
4. R. L. Ornstein, M. D. Paulsen, and M. B. Bass, "Molecular Dynamics Simulations of the Biodegradative Enzyme Cytochrome P450cam," presented at the Conference on Biodegradation of Hazardous Wastes, sponsored by NIEHS, Utah State University, Logan, Utah, April 9-10, 1990, Abstract 17.
5. M. D. Paulsen, M. B. Bass, and R. L. Ornstein, "Molecular Dynamics Simulations of Cytochrome P450cam," presented at the National AAAS Meeting, New Orleans, Louisiana, February 15-20, 1990, Abstract 22.
6. R. L. Ornstein, M. D. Paulsen, and M. B. Bass, "Molecular Dynamics Simulations of Cytochrome P450cam," presented at the Regional ACS Meeting, University of Utah, Salt Lake City, Utah, June 13-15, 1990, Abstract 15.
7. M. D. Paulsen and R. L. Ornstein, "Molecular Dynamics Simulations of Cytochrome P450cam," presented at the 7th International Symposium on Microsomes & Drug Oxidations, Karolinska Institutet, Stockholm, Sweden, June 25-29, 1990, Abstract 282.
8. T. L. Poulos, B. C. Finzel, and A. J. Howard, "High-Resolution Crystal Structure of Cytochrome P-450cam," *J. Mol. Biol.* 195, 687-700 (1987).
9. D. R. Nelson and H. W. Strobel, "Secondary Structure Prediction of 52 Membrane-Bound Cytochromes P-450 Show a Strong Structural Similarity to P-450cam," *Biochemistry* 28, 656-660 (1989).
10. R. L. Ornstein, "Rational Redesign of Biodegradative Enzymes for Enhanced Bioremediation: Overview and Status Report for Cytochrome P450," Proceedings of the National Research and Development Conference on the Control of Hazardous Materials, HMCRI, Silver Spring, Maryland (in press).
11. W. M. Atkins and S. G. Sligar, "Molecular Recognition in Cytochrome P-450: Alteration of Regioselective Alkane Hydroxylation Via Protein Engineering," *J. Am. Chem. Soc.* 111, 2715-2717 (1989).
12. M. B. Bass and R. L. Ornstein, "Molecular Dynamics Simulations of Cytochrome P450cam with an Alternate Substrate, Norcamphor," presented at the Symposium on *Converging Approaches in Computational Biology*, SUNY/Albany, New York, September 13-15, 1990, Abstract 23.
13. R. L. Ornstein and M. B. Bass, "Molecular Dynamics Simulations of Cytochrome P450cam with an Alternate Substrate, Norcamphor," presented at the ACS North Carolina Annual Symposium: Challenges in Computational Chemistry, Raleigh, North Carolina, September 14-15, 1990, Abstract 5.

4. Molecular Science Software

R. A. Bair, D. F. Feller, R. A. Kendall, and T. H. Dunning, Jr.

The Molecular Science Software project focuses on the application of advanced theoretical methodologies, computational techniques, computer technologies, and computer architectures to molecular science to develop a new generation of software to address the complex molecular problems found in environmental chemistry. The current effort addresses areas where significant advances in software technology are needed to enable the Environmental and Molecular Sciences Laboratory (EMSL) to fulfill its research mission. The areas of research and development actively being pursued are advanced computer architectures, graphics and visualization, and molecular databases. The sections below describe the accomplishments in the first two areas; work in the third area is expected to begin in FY 1992.

At the end of FY 1990, PNL joined with the California Institute of Technology (Caltech), Rice University, Argonne National Laboratory, and a number of other universities and national laboratories to form the Concurrent Supercomputer Consortium. The objective of the consortium is to acquire a state-of-the-art massively parallel computer and use it in leading-edge scientific computations.

The machine being acquired by the consortium is a one-of-a-kind prototype developed by Intel Scientific Computers with very large scale integration (VLSI) routing technology developed at Caltech by C. L. Seitz and W. J. Dally and with research support from the DARPA Touchstone Project. The Touchstone DELTA system will consist of 570 nodes; a 16-by-33 mesh of numeric nodes (each with an Intel i860 processor and 16 Mbytes of memory) and 32 disk storage nodes with an aggregate of 45,000 Mbytes of disk storage. The balance of the 570 nodes consists of two mass storage nodes (each with two 8-mm tape drives), two gateway nodes with Ethernet interfaces, and six service nodes.

This machine will be installed in the Caltech Concurrent Supercomputer Facility in April 1991. In the interim, the consortium will use a 64-node iPSC/860, Intel's current production system. The Molecular Science Software project will make extensive use of this machine to develop software and prototype codes for use on the massively parallel computer system expected to be installed in the Molecular Science Computing Facility (MSCF) and for production

computing in a number of areas, especially biomolecular and geochemical simulations, and including *ab initio* electronic structure calculations.

Computational Chemistry Codes for Advanced Computer Architectures

Computational chemistry applications require substantial computing resources. Because of the inherent limitations of uniprocessor systems, multiprocessor parallel computing will become an increasingly important tool for molecular computations. Although a parallel processor system with potentially the same computing power as a uniprocessor system is far less costly, it has proven difficult to deliver this potential savings to the user. However, work to date suggests that such multiprocessor systems can be used effectively for molecular computations and that these systems can be scaled to very high-performance levels.

Current chemistry applications do not run efficiently on parallel machines; thus, application codes must be re-engineered to take advantage of parallel architectures—a substantial undertaking. Work must also be pursued on the development of a new generation of computational chemistry codes explicitly designed for parallel machines. These codes will provide the performance needed to address the most demanding molecular problems encountered in the environment.

Present plans call for the installation of a dual architecture computer system in the MSCF—a system combining the power of a modern supercomputer with the high potential of a massively parallel computer. A dual architecture computer will allow for a staged software development approach, providing a platform for current production work as well as a facile migration path for the development of algorithms that exploit the higher performance of large-scale parallelism. Efforts are also being devoted to defining the resources necessary to distribute computations between conventional and massively parallel supercomputers. Current activities are focused on the development of molecular codes for large-scale parallel computer systems.

Ab Initio Quantum Chemistry in Parallel

The granularity of most implementation methods used in *ab initio* codes are not amenable to a straightforward port to any parallel environment. The algorithm itself might be inherently parallelizable, but the implementation usually is not. Current parallelizing

compilers can handle the fine-grain parallel tasks in Fortran but cannot easily deal with the subroutine or subroutine tree level parallel tasks. These compilers do allow the programmer to put the coarse-grain tasks together but at a considerable investment in effort.

Another alternative is to completely recode in a high-level parallel language (for example, Strand). Unfortunately, few implementations and no standards exist.

To date, our attention has been focused on multiple instruction-multiple data (MIMD) architectures, with both shared and distributed memory. Since portability and efficiency are of the utmost importance, the current state of parallel languages and programming environments is being carefully evaluated. Unfortunately, those available today are lacking in many areas. All parallel implementations have some form of message-passing, informing each processor what specific portion of the work must be done. Either data or instructions or both are passed and processed concurrently.

Thus, a message-passing toolkit has been developed in conjunction with R. J. Harrison in the Theoretical Chemistry Group at Argonne National Laboratory (ANL). This toolkit was designed to be portable and easy to use. It contains the minimal set of operations required by the algorithms. These are based partially on experiences with Intel iPSC primitives and the PARMACS tools (J. Boyle and coworkers at ANL).¹ The toolkit is, at present, only supported on either true message-passing machines or UNIX-based computers.

In FY 1990, we produced a new parallel version of ARGOS, the integral generation program in the COLUMBUS software package. To date, only the two-electron integral portion has been parallelized. This step comprises nearly all the computational effort of most Hartree-Fock self-consistent field (SCF) calculations.

An effective way to parallelize the integral calculation is at the data decomposition level, where the computation of individual shells of integrals is divided among the available processors (typically one process per processor). In practice, load balancing among the processors is not achieved by the simplest approach, namely, even division of the processes. Therefore, a shared counter was added to the toolkit.² The counter permits each processor to perform a different amount of work, according to its capacity and changing system loads. With this addition, we were able to implement an

effective parallel version of ARGOS (called PARGOS).³ This shared counter allows even very dissimilar machines to be used efficiently.

For compatibility with the other modules of the COLUMBUS package, the output integral file was concatenated into a single integral file. Figure 4.1 shows the flow of the calculation; the actual path is user specified at run time.

Another useful aspect of the message-passing toolkit is that it can utilize a local area network of workstations to form a MIMD machine with relatively slow inter-processor communications. Thus, workstations that are idle at night can be effectively used for large-scale computations. Calculations of varying sizes were performed on the five available Sun SPARCstation/330 available in the MSRC. The four problems shown in Figure 4.2 have 30, 160, 110, and 101 basis functions. The water calculation has few basis functions and high symmetry while the $\text{Si}_4\text{H}_9 + \text{CaF}$ calculation has many basis functions and little symmetry. The effective

Figure 4.1. Possible paths for PARGOS.

Figure 4.2. Effective speedup of PARGOS.

speedup is shown in Figure 4.2. On the five-node system, we realize speedups of 2.6 (water), 4.3, 4.5, and 4.5 over the single-thread calculation for each of the respective test calculations. This demonstrates the effective use of the compute power of our distributed MIMD machine. However, the results on water clearly show that one should not distribute a calculation that any one of the nodes can handle very efficiently.

Graphical User Interfaces for Computational Chemistry Codes

A visual application-independent interface greatly reduces the learning time required to run a complex application while providing full access to the power of the computer system. The graphical user interface (GUI) can also be a unifying technology, combining related application modules into integrated application systems that together more completely address scientific problems of interest. Further, by basing GUIs on industry standards, it will be possible to develop interfaces that operate on a wide range of machines and that provide a seamless connection between the

user interface on a local workstation and other networked computational services (for example, high-performance computers, database servers, data acquisition systems, and experimental control systems). The interoperability features of these GUIs will enable offsite scientists to make efficient use of the computational and information resources at the EMSL through the national networks, especially NSFnet and ESnet.

Development is being planned in each of these areas, with the goal of significantly enhancing the productivity and analytical capability of the scientist and facilitating the use of complex codes by the nonexpert. However, these are emerging technologies and substantial development work remains to be done. The effort in FY 1990 focused on the process of developing prototype interfaces for electronic structure codes to begin to define the problems to be addressed. Our GUI work has strong collaborations with the user interface technology development effort in the MSRC Computing and Information Sciences program. In addition, the first of a series of workshops, "Graphical User Interfaces in Computational Chemistry," was held September 5-7, 1990. Such workshops are an integral part of focusing GUI efforts in the scientific community, as a diverse array of significant computational chemistry GUI development efforts are underway in both the academic and commercial environments.

To support MSRC research, GUIs must be developed for a wide range of molecular simulation codes. Due to the breadth of the targeted applications and the continuing pace of computational methods development, new approaches must be developed for creating GUIs; the present "handcrafted" approach effectively prevents the widespread dissemination of this technology. Assessment of GUI development tools is therefore a present and continuing activity.

Of the GUI toolkits being developed commercially, some of the most powerful are User Interface Management Systems (UIMS). A UIMS plays the dual roles of providing facilities for GUI development and mediating between an application code and a user at a graphics workstation. A UIMS should support interactive display construction, code generation, code maintenance, and engineering documentation. These systems can provide a productive software engineering environment for GUIs, minimizing detailed hand coding with trial-and-error display design, and provide a key component in the development environment of advanced computing architectures.

GUIs for Electronic Structure Codes

There are many approaches to building a GUI for an existing application. One technique involves restructuring the program around an event-driven interactive driver. This approach is most suitable when the program must respond quickly and frequently to user input. The result is a completely new application that may not be maintainable by the original authors. Many other chemistry applications take a single set of input data and produce a single output and have little need for interaction during the computation process. Such applications may be encapsulated within a user interface with little or no modification. This approach ameliorates the maintenance problem with programs being developed by other research groups. Compound tools can be created by enveloping several applications. Likewise, a sequence of functions, potentially spanning several applications, can be mediated by an interface that initiates the appropriate executions of its modules. This model was chosen for the initial prototypes and toolkit evaluations.

Most of the efforts in the GUI project for FY 1990 were directed at laying the ground work for future activities. Several UIMS for UNIX workstations and Apple's Macintosh were evaluated to determine their effectiveness in handling a project of the complexity of that envisioned for the MSRC. Under UNIX, these included TAE+, a product of NASA's Goddard Space Flight Center; ExoCode, from Expert Object Corp.; and Guide, from Sun Microsystems. Prototyper, from Smethers Barnes; HyperCard from Apple; and SuperCard, from Silicon Beach Software were tested on the Macintosh.

A working interface to VIBROTN, a batch-oriented program written by T. H. Dunning, Jr., to compute spectroscopic constants for diatomic molecules, was constructed by K. Adams, T. Desmarais, and D. Feller using TAE+ (see Figure 4.3). Although the interface was successfully completed, significant effort was required to address the shortcomings of TAE+ and some features could not be implemented exactly as designed.

At the end of this evaluation period, it was apparent that none of the currently available commercial products that were tested was capable of adequately supporting MSRC development efforts. It was concluded, therefore, that the MSRC should enter into collaborative efforts with outside vendors to develop the tools that would be needed. However, a number of new

a)

b)

Figure 4.3. Sample screens from VIBROTN graphical user interface.

commercial products are nearing completion; these products are being tracked and promising candidates will be evaluated.

In spite of the lack of tools, a prototype of a user interface to the GAMESS⁴ electronic structure package was begun on a Macintosh using SuperCard. The goal of this effort was to gain experience in writing

interfaces for computational chemistry applications that could be transferred to later work with the next generation of UIMS tools and to evaluate the human factors aspects of the interfaces that are particular to computational chemistry. SuperCard provides an interpreted environment that facilitates making changes to a nearly completed interface in response to user feedback. This effort was coordinated with a related project in the Computing and Information Sciences program. In that effort, a set of intelligent utilities is being developed that collectively can provide research and administrative assistance to MSRC scientific staff.

In FY 1991, the GAMESS interface will be moved to Apple's version of UNIX, known as A/UX. This should make it possible to add the remote job spawning/remote job monitoring feature available in a program recently written by M. MacDuff (PNL). Additional functionality, including a graphical molecule builder, will be incorporated. Some capabilities, which are most easily accomplished with shared memory and were therefore difficult to add under the traditional Macintosh operating system, will also be attempted.

Gaussian Basis Set Library

All currently available electronic structure packages designed to treat polyatomic molecules use Gaussian functions for expanding the wave function. Because the amount of computer time required depends strongly on the total number of functions, varying from N^4 to more than N^6 , considerable efforts have been made to develop basis sets that are as compact as possible but that provide maximum accuracy across a wide range of problems. As a result, there are literally hundreds of basis sets in the chemistry literature and more appear every year. Since the selection of a suitable basis set is a critical decision affecting the ultimate quality of the calculation, it is essential that the user interface provide as much assistance as possible.

As a first step, we began an effort to assemble a collection of the most widely used Gaussian basis sets into a portable application-independent library. At present, the library consists of approximately three dozen interconnected and heavily documented ASCII files, which are designed to allow easy insertion of additional sets. Because the information in the database is application independent, it is necessary to reformat the information as needed by specific applications. While the basis set library was intended to be accessed from within the GUI, in the interim an interactive retrieval program for extracting basis sets from the library was constructed that supports input formats for the following

electronic structure packages: GAMESS, Gaussian, HONDO, MELDF, ARGOS, and Messkit.

In its first implementation, the Gaussian basis set library contains a wide variety of all-electron and effective core potential basis sets, including some that are under development at the MSRC. The library includes the STO3G, 321G, 321+G, 431G, 631G, 631G**, 6311G, 6311G**, and 6311G (3df,3pd) basis sets (J. A. Pople and coworkers); the SV, SVP, DZ, DZP, cc-pVDZ, cc-pVTZ, cc-pVQZ, aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ basis sets (T. H. Dunning and coworkers); the MINI and MIDI sets (S. Huzinaga and coworkers); the Atomic Natural Orbital basis sets (J. Almlöf and P. Taylor); hyperfine property basis sets; and basis sets for use with effective core potentials (D. Chipman).

A long-term goal is to develop a database of computational results and relevant experimental data that can be used to assist people in choosing the basis set most appropriate for a given problem.

Benchmark Calculations

Benchmark studies of selected properties and/or molecular systems are an integral part of the methods and code development activities in the Molecular Science Software project. These studies are undertaken to establish the limits of current techniques and to develop the database required to assess the accuracy of given calculations.

Electron Affinities of the First Row Atoms

Anions are prominent constituents of contaminated groundwaters. However, the theoretical description of anions has proven to be one of the most difficult tasks of modern computational quantum chemistry. For example, the full range of standard variational and perturbative approaches has been applied to calculate electron affinities (EAs) with mixed success.⁵⁻⁶ The difficulties have been variously attributed to inadequacies in the basis sets and/or the wavefunctions used to perform the calculation. Accurate treatment of electron correlation is required to calculate the EA of even first row atoms and the basis sets/wavefunctions used must be chosen carefully so as not to bias the calculation toward either the neutral or the anion.

The present study is based on a sequence of basis sets that systematically increase in size and flexibility,

coupled with a series of wavefunctions that systematically account for an ever-increasing fraction of the correlation energy. The basis sets used to calculate the EAs of the first row atoms are based on basis sets explicitly optimized for correlated calculations on the neutrals.⁷ These sets were then augmented with an additional set of s-, p-, d-, ... functions optimized for atomic anions; the additional functions are substantially more diffuse than any in the neutral set. These augmented sets are flexible enough to simultaneously describe the compact neutral system and the more diffuse anion. This procedure leads to a sequence of basis sets of ordered size and level of accuracy.

The wavefunctions are multireference singles and doubles configuration interaction (MR-SDCI) wavefunctions obtained by a systematic expansion of the orbital sets included in the multiconfiguration SCF reference space. The following orbital sets are used: 2s2p (HF), 2s2p2p', 2s2s'2p2p', 2s2s'2p2p'2p'', and 2s2s'2p2p'3d.

Two levels of excitation were investigated for the MCSCF wavefunction. The first was the normal complete active space MCSCF (CAS SCF), and the other was an "n electron reduced CAS" (n-CAS) where only n electrons are allowed to occupy the non-HF valence orbitals. Of course, for the appropriate choice of n, the n-CAS wavefunction simply reduces to the full CAS wavefunction. However, a 2-CAS wavefunction reproduces the results of the full calculations quite well with substantial reductions in the total cost.

The calculated and experimental EAs for hydrogen, boron, carbon, oxygen, and fluorine for the most accurate calculations carried out to date are listed in Table 4.1. The results of the calculations for fluorine

are plotted in Figure 4.4. From the data in the table and figure, several trends can be seen. First, the most accurate calculations differ by at most 0.08 eV from the experimental EAs. This lingering discrepancy, while small, attests to the difficulty in calculating accurate EAs.

In summary, augmented correlation-consistent basis sets can be used to calculate accurate EAs at tractable levels of theory. These basis sets are sufficiently compact so as to be amenable to molecular calculations. Future plans are to extend the benchmark calculations to several molecular anions and to the second row atoms.

Ab Initio Studies of Magnetic Hyperfine Properties

The development of first-principles methods for computing magnetic hyperfine splitting constants, such as are observed experimentally by electron spin resonance (ESR)⁸ or resonant multiphoton techniques,⁹ has proven to be extremely challenging. While Hartree-Fock or low-level perturbation theory with small valence basis sets has proven useful for determining molecular structures or approximate heats of reaction, the isotropic coupling constant, A_{iso} , is often poorly reproduced at these levels of theory. Instead, highly correlated wavefunctions are required. In some cases, theory must also supply an accurate geometry as well since the structure of the radical has not been determined experimentally. This area of study provides an excellent opportunity for experimentalists and theoreticians to benefit from collaborative efforts.

Experimentalists can utilize the results of theoretical calculations to confirm the identity of the molecule whose spectra has been recorded.¹⁰ Theoreticians can

Table 4.1. Results of MR-SDCI calculations of the electron affinities (in electron volts) of first row atoms.

Basis	MCSCF Wavefunction	H	B	C	O	F
aug-cc-pVQZ	2-CAS(2s2s'2p2p'3d)	0.740	0.258	1.254	1.384	3.337
	Experimental ^(a)	0.754	0.277	1.263	1.461	3.399

(a) H. Hotop and W. C. Linberger, *J. Phys. Chem. Ref. Data*, 4, 539 (1975).

Figure 4.4. Convergence of MR-SDCI electron affinities for fluorine.

use the experimental data as a guide to further improve the quality of their calculations.

Because A_{iso} depends on the spin density at the nucleus, special attention must be paid to a balanced treatment of core and valence correlation effects. Contributions from core and valence electrons to A_{iso} are approximately equal, of opposite sign, and each is many times larger than the final answer. As a result, severe demands are placed on the quality of the wavefunction if meaningful results are to be obtained. Failure to do so can result in qualitatively incorrect conclusions about the nature of the system under study.¹¹ It is critically important to be able to estimate the errors inherent in the computational approximations that are used in the best calculation that can be performed. By developing systematic sequences of wavefunctions that in the limit approach the complete basis set, full-CI results, it will be possible to estimate the degree of convergence in the results.

To construct such a sequence of wavefunctions, a modified version of the Dunning-Kendall-Harrison¹² "correlation-consistent" basis sets were used in conjunction with MR-SDCI wavefunctions using a configuration based on second-order perturbation theory. For the largest of the correlation consistent sets, the "aug-cc-pVQZ" (see below), the only modification that proved necessary was uncontracting one additional Gaussian primitive.

These methods were applied to the F_2^- anion and C_2^+ cation, where they could be checked against fully numerical methods, thus providing some measure of the quality of the basis set expansion. The Gaussian basis set approach and the partial-wave numerical method were found to agree to within 4 mH for F_2^- (1 mH for C_2^+) at the SCF and singles CI level of theory. Hyperfine properties were likewise well described, with differences on the order of $\pm 2\%$ for both molecules. Following the inclusion of correlation

effects, the agreement with experiment was 785 G (experiment) versus 772 G (theory) for F_2 and 34 G (experiment) versus 33 G (theory) for C_2^+ . The isotropic hyperfine value of the F_2 radical was found to be very sensitive to the bond length, with a slope of $-890 \text{ G/\AA}$. Whereas, C_2^+ possessed a slope of only $13 \text{ G/\AA}$.

Although *ab initio* theory is typically able to predict experimental hyperfine spin properties to within 10% or better,¹³ over the years exceptions have been discovered. Among the most notorious is the isoelectronic set of (2B_2) radicals¹⁴ H_2CN , H_2BO , and H_2CO^+ . Application of the extended basis set, multireference CI techniques that performed well for F_2 and C_2^+ failed in the case of H_2CN to achieve even a 20% level of agreement for A_{iso} for the protons. As seen in Figure 4.5, where $A_{iso}(H)$ is plotted against Σc_i^2 (Σc_i^2 is the sum of the squares of the reference configurations in the final CI), the convergence to the full CI limit ($\Sigma c_i^2 \rightarrow 1$) is quite slow.

With extended basis sets of the kind used in the diatomic calculations, the best computed value for A_{iso} at

Figure 4.5. Proton isotropic hyperfine constant (G) in H_2CN as a function of Σc_i^2 , the sum of the squares of the reference configurations in the final CI. These calculations were performed with a DZP basis set.

the protons was -67 G , compared to experimental values that cluster about 87 G . As seen in Figure 4.6, the calculations were clearly not converged with respect to the energy selection threshold, T_E , used to determine which configurations should be treated variationally.

Despite the fact that the largest calculation included nearly 450,000 configurations, it appears that thresholds on the order of $T_E = 10^{-8}$ to 10^{-9} and CI expansions on the order of 750,000 configurations will be needed to reach convergence to the unselected results for this molecule. Hardware constraints prohibited larger CI expansions. Other methods that were explored included the restricted HF-based MCSCF + singles CI and the UHF-based QCISD(T)¹⁵ methods. The former method gave results that were qualitatively similar to restricted HF+singles CI ($\sim 55 \text{ G}$), whereas the latter produced the best agreement with experiment yielding 76 G . For the polarized double zeta (DZP) basis, a comparison of the QCISD(T) method against a sequence of MR-SDCIs indicated that the two were in good agreement even though the configurations that were explicitly treated by the two

Figure 4.6. The proton isotropic hyperfine constant (A_{iso}) in H_2CN as a function of the selection threshold (T_E) and reference space size.

methods differed substantially. It is unknown to what extent spin contamination from higher multiplicity states affects the QCISD(T) results. Future efforts in this area will be aimed at exploring the use of even larger CI expansions and the impact of using more size consistent methods, such as the averaged coupled pair function approach.

References

1. J. Boyle, R. Butler, T. Disz, B. Glickfeld, E. Lusk, R. Overbeek, J. Patterson, and R. Stevens, *Portable Programs for Parallel Processors*, Holt, Rinehart and Winston, Inc., 1987.
2. R. A. Kendall and R. J. Harrison, "Issues of Using the Existing Mass of Quantum Chemistry Software: Load Balancing in the Parallel Version of ARGOS," *Inter. J. Quantum Chem.* (in press).
3. R. J. Harrison and R. A. Kendall, "A Parallel Version of ARGOS: A Distributed Memory Model for Shared Memory UNIX Computers," *Theo. Chimica Acta* (in press).
4. M. Dupuis, D. Spangler, and J. J. Wendoloski, *National Resource for Computations in Chemistry Software Catalog*, University of California, Berkeley, California, 1980, Program QG01; and M. W. Schmidt, J. A. Boatz, K. K. Baldrige, S. Koseki, M. S. Gordon, S. T. Elbert, and B. Lam, *QCPE Bulletin*, 7, 115 (1987).
5. D. Feller and E. Davidson, *J. Chem. Phys.* **90**, 1024 (1989) and references therein.
6. C. W. Bauschlicher, Jr., S. R. Langhoff, H. Partridge, P. R. Taylor, *J. Chem. Phys.* **85**, 3407 (1985) and references therein.
7. T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
8. See, for example, L. B. Knight, Jr., E. Earl, A. R. Ligon, and D. P. Cibranchi, *J. Chem. Phys.* **85**, 1228 (1986).
9. See, for example, R. J. Miller, W. L. Glab, and B. A. Bushaw, *J. Chem. Phys.* **91**, 3277 (1989).
10. L. B. Knight, Jr., E. Earl, A. R. Ligon, D. P. Cibranchi, J. M. Bostick, E. R. Davidson, and D. Feller, *J. Am. Chem. Soc.* **108**, 5065 (1986).
11. For a discussion of the pitfalls in computing the isotropic hyperfine splitting constant, see K. W. Richman and E. A. McCullough, Jr., *J. Phys. Chem.* **92**, 2714 (1988).
12. T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
13. See, for example, C. W. Bauschlicher, Jr., S. R. Langhoff, H. Partridge, and D. Chong, *J. Chem. Phys.* **89**, 2985 (1988); and C. W. Bauschlicher, Jr., *J. Chem. Phys.* **92**, 518 (1990).
14. D. Feller and E. R. Davidson, *J. Chem. Phys.* **80**, 1006 (1984); and D. Feller and E. R. Davidson, *Theoret. Chim. Acta* **68**, 57 (1985).
15. J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.* **87**, 5968 (1987).

5. Workshops

Two workshops were held this year. A summary of the results from each workshop is provided in the following sections.

Molecular Science Computing Facility Workshop

On February 7-8, 1990, the MSRC convened a Study Committee on Computational Molecular Science. The committee consisted of 15 computational chemists, materials scientists, and biologists and was chaired by Professor Edward F. Hayes, Rice University. The committee was asked to

- examine the role of computational molecular science in DOE's environmental initiatives
- assess the computational requirements of modeling the complex molecular systems found in the environment
- determine the benefits of a computing facility devoted to molecular science

- develop recommendations for the functionality, organization, and management of an MSCF.

To provide an optimal response to the needs of the computational molecular science effort envisioned in DOE's environmental initiatives, the committee recommended the establishment of the MSCF as a user facility in the EMSL. To meet both the long- and near-term computational needs of researchers, the committee recommended that the MSCF consist of three laboratories:

- a High-Performance Computing Center to provide production computing capabilities for EMSL users
- an Experimental Computing Laboratory to assess new computer architectures that show promise for molecular calculations
- a Graphics and Visualization Laboratory to provide state-of-the-art graphics equipment for analyzing molecular simulations.

To ensure full efficient utilization of the computers in the MSCF by all EMSL users, the committee recommended that an aggressive molecular science software development project be supported as an integral part of the MSCF. This project is to support activities directed to the development of molecular codes for high-performance and cost-effective vector and/or parallel computer systems; GUIs and graphics and visualization techniques and tool kits for the efficient and effective execution and analysis of molecular computations; databases for storing, retrieving, and manipulating the results of prior molecular simulations; and modular, integrated program systems for comprehensive solutions of molecular problems.

To transfer the technology developed in the MSCF to the wider chemistry research community, the committee recommended that a vigorous postdoctoral and visiting scientist program be established as a major component of the Molecular Science Software project. Such a program will strengthen the ties between the MSCF, academia, and industry as well as boost the competitive stance of U.S. industry.

By focusing the MSCF on molecular problems related to environmental restoration, the committee believed that PNL has a unique opportunity to establish first-class hardware facilities and a world-class team of computational and computer scientists. The computer hardware will provide state-of-the-art high-performance computational and visualization capa-

bilities for molecular computations while enabling the evaluation and exploitation of promising new computer architectures. The Molecular Science Software project has the potential to revolutionize both the performance of molecular computations and the application of molecular simulations to real-world phenomena.

The report from the Study Committee, "Molecular Science Computing Facility," is available from Thom H. Dunning, Jr., Molecular Science Research Center, Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352.

Graphical User Interfaces in Computational Chemistry Workshop

On September 5-7, 1990, a workshop on GUIs in computational chemistry was held at the Battelle Seattle Research Center, Seattle, Washington. This workshop, which was sponsored jointly by the Theory, Modeling, and Simulation program and the Computing and Information Sciences program, brought together 25 chemists and computer scientists from industry, academia, and the national supercomputer centers to discuss issues of current importance in this emerging area of technology. Discussion topics included

- the characteristics of successful interfaces for computational chemistry
- the software design tools that would be needed to construct the next generation of GUIs
- special concerns of people designing GUIs for computational chemistry programs
- the potential impact of GUI technology on the way in which computational chemistry is performed.

Overall, considerable success was achieved in communicating the major application features of chemistry code systems to GUI experts and in communicating the design and engineering features of GUIs to computational chemists.

Two general recommendations emerged from this study: first, an innovative process for designing and constructing GUIs for computational chemistry codes; and second, specific proposals to exploit the strengths of the development effort planned by the MSRC.

Today, researchers active in this field have considerable talent and ideas to offer but are largely working in

isolation. To make matters even more difficult, the current generation of interface development tools available to these researchers is inadequate to address either the needs of the developers or the interoperability needs of the chemistry community. A sound approach to the generation of GUIs for computational chemistry must first start with the creation of tools to design, evaluate, and produce the needed interfaces. It must also proceed in parallel with interface design efforts so that the tool designs and the interface designs can be continually evaluated against each other.

The difficulties in creating ubiquitous and useful interfaces are formidable and will not be solved single-handedly by any institution, however large. Yet, from the discussions at the workshop, it became evident that

a need exists for a focal point in chemistry user interface development. There was a consensus that the development of both the tools and the interfaces must be formulated collectively and that the MSRC is uniquely positioned to be the focal point for this effort. Whenever possible, a coordinated plan of attack will be developed to bring to bear as much expertise as possible. This development effort also needs to be multidisciplinary, involving chemists, computer scientists, design engineers, and human factors experts.

The report from the workshop is available from Raymond A. Bair, Molecular Science Research Center, Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352.

Computing and Information Sciences

Computing and Information Sciences

E. W. Pearson

The Computing and Information Sciences program includes both design and implementation of the computational environment for the Environmental and Molecular Sciences Laboratory (EMSL) and research in the areas of parallel computing, graphical user interfaces (GUIs) and visualization, scientific information management, and laboratory automation. The system design work is being conducted through a formal engineering process, coupled with extensive prototyping of major system components. These prototypes will be used and evaluated by Molecular Science Research Center (MSRC) staff in interim facilities; their conclusions will be used in the engineering design process. The research program is directed towards areas in which currently available computer and information technology is inadequate to support MSRC plans.

The Computer and Information Sciences program is a full-fledged partner with the physical science projects in the MSRC. Through this partnership, the productivity of both MSRC staff and technical visitors will be enhanced.

Parallel Computing

In FY 1990, two parallel computing tasks were emphasized: 1) analysis of computational chemistry algorithms to determine the potential for parallel implementation and 2) the design, analysis, and implementation of a parallel eigensolver, using a modified Jacobi algorithm. The resulting algorithm is applicable to relatively small ($O 10^2$ - 10^3) but dense matrices on highly parallel computers. A detailed and very successful timing model for this algorithm, incorporating system size, processor count, and other machine parameters was developed and validated (Figure 1.1).

In FY 1991, analysis of chemistry algorithms will continue, directed at both the selection and development of parallel algorithms and the development of a model that can be used to guide the design of a machine highly optimized for computational chemistry. Work on parallel eigensolvers will also proceed, focusing on alternative algorithms for dense systems and large, sparse systems.

Figure 1.1. Timing model.

A white paper on these issues has been drafted. It clarifies the design goals for a high-performance computer optimized for computational chemistry applications and lists the software engineering tools and operating system capabilities required to support the large-scale code development effort for the Molecular Science Software project described elsewhere in this document.

Graphical User Interfaces and Visualization

Activities during FY 1990 included development of prototype GUIs for computational chemistry codes, preparation of a white paper on technical issues in user interfaces and visualization, evaluation of software engineering tools for user interface development, and organization of a workshop on GUIs for computational chemistry. Prototyping experience and evaluation of software tools^{1,2} led to the conclusion that currently extant user interface management systems

are inadequate to support development of good interfaces for complex scientific codes without unreasonable effort.

The *Graphical User Interfaces in Computational Chemistry* workshop was held September 5-7, 1990. Participants included both computational chemists and computer scientists. The workshop addressed several topics, including the role of graphical user interfaces in computational chemistry, the state of the art in the required supporting software technologies, and priorities for research and development. The report from the workshop is available from Raymond A. Bair, Molecular Science Research Center, Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352.

Scientific Information Management

The subject of scientific information management has two components: scientific data structures and personal information management. This year, development concentrated on personal information management. Work

began on electronic information management using the "laboratory notebook" paradigm (Figure 1.2). A white paper on technical issues in scientific information management was also completed. Three usable prototypes were produced: a user interface to the GAMESS computational chemistry code, an automated process for interactive monitoring of GAMESS running on a remote computer, and a first version of the electronic laboratory notebook.

During FY 1991, work will concentrate on incorporating meta-data into general scientific data structures and on the issues associated with data interoperability.

Laboratory Automation

Implementation work this year concentrated on two systems: a personal computer-based data system for a Bruker time-of-flight mass spectrometer and a UNIX VME-based data system for an ion cyclotron resonance spectrometer located at Rice University. Both projects are scheduled for completion during early FY 1991.

Figure 1.2. EMSL Electronic Laboratory Notebook.

Additional work included the preliminary design of a microchannel plate detector for the MSRC large molecule mass spectrometer system and planning for the EMSL Interface Development Laboratory.

References

1. K. J. Adams and J. J. Thomas, "PNL Experience Using TAE+ - A Rapid Prototyping Tool," presented at the SIGCHI Conference, Seattle, Washington, April 6, 1990.

2. K. J. Adams, "Upgrading User Interface to Computational Chemistry Codes," presented at the TAE Conference, Houston, Texas, June 5, 1990.

Acknowledgments

We wish to express our appreciation to Paul Messina and the staff of the California Institute of Technology Supercomputing Facility for providing facilities to develop and test parallel codes.

1
2
3

1
2
3

Appendixes

Appendix A

MSRC Staff and Associates

Appendix A

MSRC Staff and Associates

MSRC Staff

Dr. Michael L. Knotek is the Manager of the MSRC and the EMSL, and he is the Senior Science Director for PNL. From 1985 to 1989, Knotek chaired the National Synchrotron Light Source, a DOE user facility at Brookhaven National Laboratory. Previously, Knotek was affiliated with Sandia National Laboratories; Naval Weapons

Centers at Corona and China Lake, California; and Ames Laboratory at Iowa State University. In 1984, Knotek was recognized by DOE's 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, University of Cambridge, 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; a member of the Program Review Panel for the Advanced Light Source at Lawrence Berkeley Laboratory; and a member of the American Physical Society Panel on Public Affairs and the Division of Condensed Matter Physics Strategic Planning Committee. He is also on the board of directors of the Idaho Research Foundation, Inc., and the Washington Technology Centers. He has published 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's Deputy Manager for Programs. 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 organic 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 Manager of the Environmental and Molecular Sciences Laboratory project. Previously, he was Manager of Research Operations and Services for the MSRC. Prior to that, he 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 free surface and interface materials problems both practical (applied) and fundamental.

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 also 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 first-wall neutron sputtering and plasma/wall interactions in Tokamak plasma machines.

Thomas is 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, the American Association for the Advancement of Science, and the National Association of Corrosion Engineers. He received his Ph.D. in solid-state physics/surface physics from Brown University.

Thomas has written more than 40 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 papers on the application of surface science techniques to study problems in tribology and numeral processing.

Chemical Structure and Dynamics

Dr. Steven D. Colson became Associate Director for the MSRC's Chemical Structure and Dynamics group in 1989. Between 1968 and 1989, Colson progressed from Assistant Professor to Professor of Chemistry at Yale University. Colson has authored or co-authored 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. From 1985 to 1987, he was a mem-

ber 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 and the Optical Society of America. Recently, Colson was awarded a Humboldt Fellowship, for studies in Munich, in recognition of his past accomplishments in research and teaching.

Dr. Richard S. Blake is a Senior Research Scientist specializing in the application of time-resolved and nonlinear optical laser methods to the study of the chemical dynamics of interfaces. Prior to joining the MSRC, he was a Graduate Research Assistant at Stanford University, where he conducted studies of funda-

mental reaction dynamics by applied nonlinear laser techniques.

As a Summer Research Fellow in the Physical Sciences Department of Du Pont Experimental Station, Wilmington, Delaware, Blake studied catalytic methanol decomposition on zeolitic surfaces by Fourier transform infrared spectroscopic methods. As an undergraduate Research Assistant at Hope College, he performed spectroscopy of substituted aromatics in low-temperature glasses and supersonic molecular beams by two-photon laser spectroscopic techniques.

Blake was awarded a Kosciuszko Foundation Fellowship in 1978, a Presidential Scholarship in 1979, a National Science Foundation Undergraduate Research Program Fellowship in 1981, the Kleinheksel Mathematics Award in 1980, the American Chemical Society Analytical Chemistry Award in 1981, and the Almon T. Godfrey Prize in Chemistry in 1982. Blake is a Phi Beta Kappa and graduated from Hope College *summa cum laude*.

Blake received his Ph.D. in physical chemistry in 1988 from Stanford University, where he was a member of the research group led by Professor Richard N. Zare. His doctoral dissertation was presented on "Quantitative Fundamental Reaction Dynamics: The $H + D_2 \rightarrow HD + D$ Reaction." He is a member of the American Chemical Society, the Optical Society of America, the American Physical Society, the Institute of Electrical and Electronics Engineers, and the Lasers and Electro-Optics Society. He has written four papers on experimental investigations of chemical reaction dynamics.

Dr. James P. Cowin is a Senior Research Scientist in the Chemical Structure and Dynamics group. 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 intramolecular charge-transfer dynamics at solid/liquid interfaces using the ultrafast laser multiphoton-ionization mass spectrometry and resonance Raman spectroscopy capabilities available at PNL. 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 Univer-

sity 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 contributed to the development of new formalisms for understanding the nonlinear interactions of free molecules with laser light.

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 group 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 and is a member of the American Chemical Society and the American Physical Society. He has written or co-authored a dozen publications on topics such as photodissociation dynamics, photofragment imaging, radical kinetics, and Raman spectroscopy and has made numerous presentations at 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 group, 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 authored or co-authored 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.

Dr. Robert J. Miller joined PNL in 1988 as a Senior Research Scientist in the Atomic and Molecular Chemistry Section. His principal research interests involve elucidation of the structural and dynamical properties of excited electronic states of small molecules using ultrahigh-resolution multiple-resonance laser spectroscopy.

This research continues a collaboration with Dr. S. D. Colson that began while they were both at Yale University.

While a faculty member of the Department of Chemistry, Michigan Technological University, Miller held appointments as a Visiting Fellow at Yale University during 1986 and for the 1987-1988 academic year. He also has been Guest Professor at the Max-Planck-Institute for Polymer Science in Mainz, Germany, where he pursued research in stochastic nonlinear optics.

As a Postdoctoral Fellow with Professor Gerhard L. Closs in the Department of Chemistry, University of Chicago, Miller pioneered the use of nuclear magnetic resonance (NMR) detection in laser flash photolysis investigations of the kinetics of radicals, biradicals, and triplet states and of the dynamics of spin polarization phenomena.

Miller received his Ph.D. in chemistry from Ohio State University. He is a member of Sigma Xi, the American Physical Society, the American Chemical Society, and the American Association for the Advancement of Science. He has published papers in the fields of laser spectroscopy and NMR spectroscopy and has presented invited seminars at universities throughout the United States and Europe. He recently contributed papers to the Gordon Research Conferences on Magnetic Resonance and on Multiphoton Processes.

Dr. Steven W. Sharpe is a Senior Research Scientist in the Chemical Structure and Dynamics group. He received his Ph.D. in physical chemistry from the State University of New York at 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 discusses advances in molecular vibrations and collisional dynamics.

Environmental Dynamics and Simulation

proton-induced x-ray emission, x-ray diffraction, infrared, and other spectroscopic techniques to characterize

Dr. James E. Amonette is a Research Scientist in PNL's Earth and Environmental Sciences Center and part of the team responsible for the 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

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, synchrotron-based x-ray diffraction, and scattering studies of soil materials.

opment and application of reactive chemical transport models that include the effects of advection, disper-

Dr. Charles J. Hostetler is a Senior Research Scientist in PNL's Earth and Environmental Sciences Center (EESC) and is a member of the EESC liaison team to the MSRC. Since joining PNL, he has been involved in applications of geochemistry to contaminant transport. Hostetler's primary contribu-

tions have been in 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 authored or co-authored 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 leads the MSRC's Macromolecular Structure and Dynamics group. Prior to joining PNL in 1988, he spent 16 years at Lawrence Berkeley Laboratory, most recently as leader of the Environmental Physiology group in the Biology and Medicine Division. 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, the American Conference of Governmental Industrial Hygienists, and the IEEE Committee on Man and Radiation.

He chairs the COMAR ELF/VLF subcommittee and the National Research Council committee on the potential health effects of electromagnetic radiation from the Air Force's Ground Wave Emergency Network.

Tenforde has authored or co-authored 160 publications and has presented 60 invited lectures at conferences and symposia during the last 10 years. Recent invited lectures include talks at the International Union of Radio Sciences Twenty-Third General Assembly in Prague, Czechoslovakia, and the Bioelectrical Repair and Growth Society's Tenth Annual Conference in Philadelphia.

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 (UC-B) from 1963 to 1968 and received his Ph.D. in biophysics in 1969. Tenforde was a Bay Area Heart Research Committee Postdoctoral Fellow at UC-B from 1969 to 1971 and an NIH Postdoctoral Fellow from 1971 to 1973.

Dr. Richard D. Smith, Senior Staff Scientist, leads PNL's Chemical Methods and Separations group and directs research related to the development of new instrumentation, supercritical fluid solvation phenomena, mass spectrometry (MS), and novel separation processes. For the past 5 years, his research has centered on the fundamental

aspects and applications of MS and the development of new analytical instrumentation, particularly related to large molecule characterization.

Smith has been the principal investigator for programs studying 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-MS (1983), the development of the first direct interface combining capillary zone electrophoresis with MS (1988), and a process for materials formation from supercritical fluids (1988). In 1988, he patented processes for forming fine powders and thin films from supercritical solutions. He has presented more than 100 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. He is a member of the American Chemical Society, the American Society for Mass Spectrometry, the American Society for Testing and Materials, and the American Association for the Advancement of Science. Smith has been awarded six patents and has authored or co-authored more than 200 papers on MS, separation processes, and supercritical fluids and their application to materials processing and separation methods.

Materials and Interfaces

Dr. Gary L. McVay is Manager of PNL's Materials Sciences Department and Deputy Manager of the MSRC. He joined PNL in 1978 as a research scientist and has held positions of increasing responsibility since then. McVay's areas of specialization include ionic mobilities in glass; interactions of ceramic materials with aqueous

solutions and the effects of radiation on these interactions; structural water effects on silicate properties; defect mobilities and diffusional properties in semiconductor materials; and neutron irradiation-induced deformation in metals.

Prior to joining PNL, McVay was with the solid-state physics research section at Sandia National Laboratories and the EBR-II site at Idaho Falls, Idaho. He received his Ph.D. in ceramic engineering from the University of Missouri in 1970.

McVay is coordinator of the Materials Sciences' Basic Energy Sciences programs at PNL. He is a member of the American Ceramics Society, American Nuclear Society, Materials Research Society, Pacific Northwest Materials Council, Materials Directors' Council, and Advisory Committee of the Washington Technology Center. He currently has 61 open literature publications, has presented numerous invited papers, and was the editor of five proceedings documents.

Dr. Donald R. Baer is a Senior Research 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 and is secretary of the Applied Surface Science Division and Associate Editor of the *Journal of Vacuum Science and Technology A*. He is 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 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, Illinois, between 1974 and 1976. He has authored or co-authored more than 75 publications.

Theory, Modeling, and Simulation

Dr. Thom H. Dunning, Jr., joined the MSRC as Associate Director for Theory, Modeling, and Simulation in 1989. From 1978 to 1989, he was Senior Scientist, Group Leader of the Theoretical and Computational Chemistry Group, and Head of the Chemical Dynamics Program at Argonne National Laboratory (ANL). Dunning is

an Affiliate Professor at the University of Washington and an Adjunct Professor at Washington State University.

Often an invited speaker, Dunning's presentations in 1989 included lectures at numerous universities, the Idaho National Engineering Laboratory's Computational Chemistry Seminar, ANL's Workshop on "Methodology for the Evaluation of Molecular Integrals, and American-Japanese Information Exchange Seminar (Honolulu, Hawaii). He has authored or co-authored more than 80 publications on topics ranging from

theoretical studies of the excited states of organic molecules to reaction-path analysis of molecular potential energy surfaces.

Dunning is a member of the American Chemical Society, the American Physical Society, and the American Association for the Advancement of Science. Since 1987, he has been Series Editor for *Advances in Molecular Electronic Structure Theory* published by JAI Press, Inc. His committee memberships include DOE's Executive Committee of the Energy Research Supercomputer Users' Group and the panel that drafted the Energy Research document, "Basic Research for Environmental Restoration." Dunning is currently Vice President of the Advisory Board of the Foundation for Chemical Research, Department of Chemistry, University of Missouri-Rolla.

Dunning was awarded a Woodrow Wilson Fellowship (1965) and a National Science Foundation Predoctoral Fellowship (1966-1969). He received his Ph.D. in chemistry from the California Institute of Technology in 1969.

Dr. Raymond A. Bair joined the MSRC's Molecular Science Software project as a Staff Scientist and Technical Group Leader in 1990. 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 molecular data bases.

From 1987 to 1990, Bair was director of new product development with BIODESIGN, Inc., a small startup company in Pasadena, California. BIODESIGN

produces interactive molecular modeling 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 chemical reactions and developed *ab initio* computational methods for attached processors and 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 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. David F. Feller recently joined the MSRC as a Senior Research Scientist. 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 investiga-

tion of ground 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.

Feller has authored or co-authored 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.

Dr. Bruce C. Garrett joined the MSRC as a Senior Research Scientist and Group Leader in 1989. From 1980 to 1989, he was a founder and research scientist at Chemical Dynamics Corporation, where he developed and directed basic research in theoretical physical chemistry. For more than 15 years, Garrett has been engaged in research

involving theoretical and computational chemistry, particularly in the field of the dynamics of atomic and molecular collisions. Since 1977, Garrett has been a key participant in the development of practical and reliable methods for predicting rate constants for gas-phase chemical reactions. He has authored or co-authored 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.

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. During 1990, he has been an invited speaker at Washington State University, the Symposium on The Reaction Path in Chemistry at the 199th American Chemical Society National Meeting, and the NATO Advanced Studies Institute on Theoretical and Computational Models for Organic Chemistry in Porto Novo, Portugal. For the last year, he served as a committee member of the National Research Council Review Panel for the AFOSR High Energy Density Materials program.

Dr. Rick A. Kendall, a Senior Research Scientist in the Molecular Science Software project, specializes 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. Kendall graduated *magna cum laude* from Indiana State University in 1983 and is 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 University of Utah in 1988.

Kendall is a member of the American Chemical Society and the American Physical Society. He has authored or co-authored papers and made presentations that describe 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.

Dr. John P. LaFemina joined the MSRC as a Senior Research Scientist in 1989 and is currently a Group Leader. His research seeks a comprehensive understanding of the atomic and electronic structure, including atomistic dynamics, of insulator and semiconductor surfaces important in areas as diverse as the design of advanced electronic materials and subsurface contaminant transport. Between 1985 and 1989, LaFemina was a Captain in the United States Army at the United States Military Academy, serving as a Deputy Director of the Academic Research Division. The Division is a faculty research center consisting 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 research interests include modeling the electronic 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 Pennsylvania State University under the direction of Dr. John P. Lowe in 1985. He has authored or co-authored more than 40 papers and presentations on topics ranging from the photophysics of polyimide and poly(ethylene terephthalate) to the atomic and electronic structure of mineral oxide surfaces. He is a member of the American Chemical Society, the American Physical Society, the American Vacuum Society, and the Materials Research Society.

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. 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 and lecturer at Princeton University in the Biochemistry Department.

After receiving his Ph.D. in Biophysical Sciences from the State University of New York at 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. Ornstein was awarded fellowships during his master's, doctoral, and postdoctoral studies.

During the last two years, Ornstein has given 16 invited seminars at universities and conferences throughout the United States. He has published papers in the areas of molecular mechanics/dynamics force field validation for nucleic acids and proteins, applications of molecular mechanics methods to the study of structure/function relationships of nucleic acids and their interactions with ligands that intercalate or form adducts, and applications of molecular mechanics/dynamics methods to the study of structure/function/dynamic relationships of peptides, proteins, and biodegradative enzymes.

Dr. Douglas Ray joined the MSRC's Theory, Modeling, and Simulation group as a Senior Research Scientist in 1990. Previously, he was a Postdoctoral Research Associate at the Joint Institute for Laboratory Astrophysics in Boulder, Colorado, and a Research Assistant at the University of California-Berkeley.

Ray received his Ph.D. in physical chemistry in 1985 from the University of California-Berkeley, where his advisor was Richard J. Saykally. He has written or contributed to more than a dozen publications on topics such as ultrafast time-resolved dynamics in mass selected clusters and has been invited to lecture at gatherings such as the 5th International Symposium on Small Particles and Inorganic Clusters in Konstanz, Germany, in 1990.

Dr. Gregory K. Schenter joined the MSRC in 1988 after receiving his doctoral degree. While he pursued his education, he held various positions and gained experience in both basic and applied physics. His current interests include the theoretical modeling of chemical dynamics occurring in the condensed phase. In 1984,

Schenter developed an analysis of fission product yield data at Los Alamos National Laboratory. Between 1981 and 1983, he performed reactor physics calcula-

tions and modeled material flows and production for United Nuclear Industries. In 1980, he did computer modeling of dye laser physics and uranium enrichment systems for Exxon Nuclear Company. Between 1978 and 1979, he performed statistical evaluations of nuclear decay heat data for Westinghouse Hanford Company.

Schenter received his Ph.D. in applied physics from Cornell University. His Ph.D. thesis presented "A Unified View of Classical and Quantum Kinetic Theory with Applications to Charge-Carrier Transport in Semiconductors." He has also written 10 papers in the areas of nuclear, plasma, and semiconductor physics.

Computing and Information Sciences

Dr. Erik W. Pearson leads the Computing and Information Sciences group. He also heads the Applied Computational Mathematics group in the PNL's Applied Physics Center. Pearson was a Post-doctoral Fellow at PNL in 1983 and joined the staff in 1984. He is responsible for developing capabilities in the areas of computational modeling and scientific computing. Pearson leads PNL's work in scientific parallel computing. His current research interests include nonlinear dynamics and atmospheric chemistry.

Earlier work includes development of a model for the index of refraction of ionic crystals, modeling of electric dipoles induced in intermolecular collisions, and a novel treatment of density functional expansions for the kinetic energy of an inhomogeneous electron gas. He was also responsible for the management of the data acquisition, management, and analysis functions of a major project.

Pearson received his Ph.D. in chemical physics at Harvard University in 1983. He is a member of the American Association for the Advancement of Science, the American Geophysical Union, the American Physical Society, and the Society for Industrial and Applied Mathematics. He has authored or co-authored more than a dozen publications.

James J. Thomas is the Chief Scientist for the Computing and Information Sciences program, specializing in the research, design, and implementation of information systems at PNL. His work is known nationwide, and he has earned three international science awards as a leader in information systems. Thomas has been a primary investigator in programs such as molecular science information architecture, computer-aided genetic engineering, ASHRAE building code standard system, analysis of large data sets, mobile data acquisition and analysis system, distributed interactive graphics system, information retrieval and plotting system, energy recording data acquisition and analysis system, radiological sciences monitoring system, under-

sodium viewing project, compiler design, and operating system support.

Thomas is currently chair of SIGGRAPH and served as vice chair from 1987-1989. He was the co-chair of the organization's 1987 international conference (attended by over 30,000 people with a budget of \$5 million) and was technical program chair for the 1980 conference for interactive graphics. SIGGRAPH is a special interest group on graphics of the Association of Computing Machinery, a 13,000-member international organization. He has been a member of the editorial staff for *Computer Graphics Journal* and served on the editorial board for *Transactions on Graphic Systems*.

Thomas received his M.S. in computer science from Washington State University. He has written more than 50 papers on advanced graphics technology and its applications.

MSRC Associates

Dr. Gregory E. Arnold.

Postdoctoral Appointee - Theory, Modeling, and Simulation.

Ph.D., Biochemistry, Washington State University, 1989 (mentor: 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; B.A., Chemistry, Johns Hopkins University, 1983.

Dr. Michael B. Bass.

Postdoctoral Appointee - Theory, Modeling, and Simulation.

Postdoctoral Fellow (Muscular Dystrophy Association Fellowship), Institute of Neuroscience, University of Oregon, 1987-1989 (advisor: Monte Westerfield); Ph.D.,

Biochemistry, Iowa State University, 1987 (advisor: Herbert J. Fromm); B.S., Biochemistry and Biophysics, Oregon State University, 1982.

Dr. Thomas J. Godin.

Postdoctoral Appointee - Theory, Modeling, and Simulation.

Ph.D., Physics, University of Oregon, 1988; M.S., Physics, University of Oregon, 1984; B.S., Mathematics, University of Rhode Island, 1982.

Dr. Kenneth M. Beck.

Postdoctoral Appointee - Chemical Dynamics and Structure.

Postdoctoral Fellow, Chemical Physics, University of Pennsylvania, 1988-1990 (advisor: Marsha I. Lester); Ph.D., Physical Chemistry, University of Illinois-Chicago,

1988 (advisor: Robert J. Gordon); M.S., Chemistry, University of Illinois-Chicago, 1984; B.A., Astronomy/Physics, Northwestern University, 1972.

Dr. Anthony C. Hess.

Postdoctoral Appointee - Chemical Dynamics and Structure.

Ph.D., Chemistry, Arizona State University, 1988; B.S., Chemistry, North Dakota State University, 1984.

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. Rachel Ogorzalek-Loo.

Postdoctoral Appointee - Chemical Dynamics and Structure; Chemical Methods and Separations.

Ph.D., Physical Chemistry, Cornell University, 1989; M.S., Physical Chemistry, Cornell University, 1984 (advisor: Paul Houston); B.S. Chemistry, University of Wisconsin-Madison, 1981.

Mlu Kwini.

Graduate Student - Chemical Dynamics and Structure.

Ph.D. Candidate (1991), Physical Chemistry, University of California-Santa Barbara.

Dr. Mark D. Paulsen.

Postdoctoral Appointee.

Ph.D., Physical Chemistry, University of Wisconsin-Madison, 1989 (advisor: M. Thomas Record); B.S., Chemistry, University of Nebraska-Lincoln, 1982.

Dr. Robin P. McRae.

Faculty Intern, University of Utah, 1990.

Ph.D., Chemistry, University of California-Berkeley, 1989 (advisor: A.D.J. Haymet); B.S., Mathematics/Chemistry, University of Puget Sound, 1985.

Dr. Andrew J. Skinner.

Postdoctoral Appointee - Materials and Interfaces.

Ph.D., Theoretical Solid State Physics, Imperial College, University of London, UK, 1989; First Class B.Sc., Mathematics, Imperial College, University of London, 1985.

Dr. Scott Smith.

Postdoctoral Appointee -
Chemical Dynamics and
Structure.

Ph.D., Chemistry, University
of Utah, 1988; B.S., Chemis-
try, Northern Arizona Uni-
versity, 1983.

Dr. Sotiris S. Xantheas.

Postdoctoral Appointee -
Theory, Modeling, and
Simulation.

Ph.D., Physical Chemistry,
Iowa State University, 1990
(advisor: Klaus Ruedenberg);
Diploma, Chemical Engineer-
ing, National Polytechnic
University of Athens, Greece,
1984.

Dr. Mark O. Trulson.

Postdoctoral Appointee -
Chemical Dynamics and
Structure.

National Institutes of Health
Fellow, Massachusettes Insti-
tute 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.

Appendix B

FY 1990 Publications and Presentations

Appendix B

FY 1990 Publications and Presentations

Publications

- G. Arjavalingam, G. Hougham, and J. P. LaFemina, "Emission Mechanism in Polyimide," *Polymer* **31**, 840 (1990).
- D. R. Baer, D. L. Blanchard, M. H. Engelhard, and J. M. Zachara, "The Interaction of Water and Mn with Surfaces of CaCO_3 : An XPS Study," *Surface and Interface Analysis* (in press).
- K. M. Beck, M. T. Berry, M. R. Brustein, and M. I. Lester, "The Vibrational Overtone Spectroscopy of OH-Ar Complexes," *Chem. Phys. Lett.* **162**, 203-210 (1989).
- K. M. Beck and R. J. Gordon, "Vibrational Relaxation of Highly Excited SiF_4 and $\text{C}_6\text{F}_5\text{H}$ by Ar," *J. Chem. Phys.* **92**, 6011-6016 (1990).
- D. L. Blanchard, D. L. Lessor, J. P. LaFemina, D. R. Baer, W. K. Ford, and T. Guo, "A LEED Study of the $\text{MgO}(001)$ Surface Structure," *J. Vac. Sci. Tech.* (in press).
- E. G. Chapman, C. J. Barinaga, H. R. Udseth, and R. D. Smith, "Confirmation and Quantitation of Hydroxymethanesulfonate in Precipitation by Electrospray Ionization-Tandem Mass Spectrometry," *Atmospheric Environment* **24A** (in press).
- D. C. Chatfield, R. S. Friedman, D. G. Truhlar, B. C. Garrett, and D. W. Schwenke, "Global Control of Suprathreshold Reactivity by Quantized Transition States," *J. Am. Chem. Soc.* (in press).
- J. Cook, G. R. Holtom, and P. Lu, "Detection of Protein-DNA Complex Formation by Time-Resolved Fluorescence Depolarization of Bound Ethidium Bromide," *Anal. Biochem.* **190**, 331 (1990).
- L. S. Dake, D. R. Baer, K. F. Ferris, and D. M. Friedrich, "Ligand and Structure Effects on the Nitrogen-Phosphorus Bonds of Phosphazenes," *J. Electron Spectrosc. Relat. Phenom.* **51**, 439-57 (1990).
- J. T. Dickinson, S. C. Langford, L. C. Jensen, L. R. Pederson, and D. R. Baer, "Consequences of Simultaneous Exposure of Inorganic Solids to Excimer Laser Light and an Electron Beam," *J. App. Phys.* **68**, 1831-1836 (1990).
- C. B. Duke, D. L. Lessor, T. Guo, and W. K. Ford, "Low-Energy-Electron-Diffraction Intensity Analysis of the Atomic Geometry of $p(1 \times 1)$ Monolayers of Bismuth on $\text{GaAs}(110)$," *J. Vac. Sci. Tech.* **A8**, 3412 (1990).
- C. G. Edmonds, J. A. Loo, S. M. Fields, C. J. Barinaga, H. R. Udseth, and R. D. Smith, "Capillary Electrophoresis Combined with Electrospray Ionization Mass Spectrometry and Tandem Mass Spectrometry," in *Biological Mass Spectrometry*, A. L. Burlingame and J. A. McCloskey, eds., Elsevier, 1990, p. 77-100.
- C. G. Edmonds and R. D. Smith, "Electrospray Ionization Mass Spectrometry," *Methods in Enzymology: Mass Spectrometry* (in press).
- C. G. Edmonds and R. D. Smith, "Mass Spectrometry, DNA Sequencing and the Human Genome Initiative," *ACS Division of Anal. Chem. Newsletter*, 27-34 (1990).

C. G. Edmonds, R. D. Smith, and L. M. Smith, "The Relevance of Mass Spectrometry to DNA Sequence Determination: Research Needs for the Human Genome Program," PNL-SA-18079 (CONF-9004251), Pacific Northwest Laboratory, Richland, Washington, 1990.

D. Feller, "An *Ab Initio* Study of the Hyperfine Properties of F_2^+ (C_2^+)," *J. Chem. Phys.* **93**, 579 (1990).

D. Feller and E. R. Davidson, "Basis Sets for *Ab Initio* MO Calculations," *Reviews in Computational Chemistry*, K. B. Lipkowitz and D. B. Boyd, VCH Publishers, New York, 1990.

D. Feller and E. R. Davidson, *J. Chem. Phys.* **90**, 1024 (1989).

D. Feller and E. R. Davidson, "Theoretical Approach to ESR Spectroscopy," a chapter in *Theoretical Models of Chemical Bonding*, Springer Verlag (in press).

W. K. Ford, T. Guo, S. L. Lantz, K. Wan, S.-L. Chang, C. B. Duke, and D. L. Lessor, "Bi and Sb Adsorption on III-V(110) Substrates: Growth, Order and Structure," *J. Vac. Sci. Tech.* **B8**, 940 (1990).

W. K. Ford, T. Guo, D. L. Lessor, and C. B. Duke, "Dynamical LEED Analysis of Bi and Sb Epitaxy on GaAs(110)," *Phys. Rev. B* (in press).

B. C. Garrett, M. L. Koszykowski, C. F. Melius, and M. Page, "Theoretical Calculations of the Thermal Rate Constants for the Gas-Phase Chemical Reactions $H + NH_2 \rightarrow H_2 + NH_2$ and $D + ND_3 \rightarrow D_2 + ND_2$," *J. Phys. Chem.* **94**, 7096 (1990).

B. C. Garrett and C. F. Melius, "Variational Transition State Theory Calculations of Tunneling Effects on Concerted Hydrogen Motion in Water Clusters and Formaldehyde/Water Clusters," in *Proceedings of the NATO Advanced Studies Institute on Theoretical and Computational Models for Organic Chemistry*, Kluwer Academic Publishers (in press).

T. L. Gilton, J. P. Cowin, G. Kubiak, and A. Hamza, "Intense Surface Photoemissions: Charge Effects and Self-Acceleration," *J. Appl. Phys.* (in press).

T. L. Gilton, C. Dehnhostel, and J. P. Cowin, "Electron Transmission Probability Through Layers of H_2O and Xe in the UHV Photoreduction of CH_3Cl on Ni(111)," *J. Chem. Phys.* **92**, 1937 (1989).

T. L. Gilton, C. Dehnhostel, M. R. Schneider, and J. P. Cowin, *J. Chem. Phys.* **91**, 1937 (1989).

E. E. Gulcicek, S. D. Colson, and L. D. Pfefferle, "Multi-Photon Ionization Detection of Methyl Radicals from Catalytic Oxidation of Methane," *J. Phys. Chem.* **94**, 7069 (1990).

E. E. Gulcicek, S. D. Colson, and L. D. Pfefferle, *Rev. Sci. Instrum.* (in press).

J. R. Guth, A. C. Hess, W. T. Petuskey, and P. F. McMillan, "Ab Initio Force Field for Diamond," *J. Phys. C* (in press).

S. G. Hansen, G. Luckman, G. C. Nieman, and S. D. Colson, "Laser-Induced Fluorescence Study of CF Radicals in CF_4/O_2 Plasmas," *J. Vac. Sci. Tech.* **B8**, (2):128 (1990).

S. G. Hansen, G. Luckman, G. C. Nieman, and S. D. Colson, "Formation and Decay of Metastable Fluorine Atoms in Pulsed Fluorocarbon/Oxygen Discharges Monitored by Laser-Induced Fluorescence," *Appl. Phys. Lett.* **56**, (8):719 (1990).

- M. Hawley, T. L. Mazely, L. K. Randeniya, R. S. Smith, X. K. Zeng, and M. A. Smith, "A Flow Jet Reactor for Ion-Molecule Reaction Studies at Very Low Energies," *Int. J. Mass Spectrum Ion Processes*, **97**, 55 (1990).
- G. R. Holtom, "Artifacts and Diagnostics in Fast Fluorescence Measurements," SPIE Proceedings **1204**, *Time-Resolved Laser Spectroscopy in Biochemistry II*, 2 (1990).
- G. R. Holtom, "Experimental Time-Resolved Methods," in *Photon Migration in Tissues*, B. Chance, ed., Plenum Press, New York, 1990, p. 139.
- S. A. Kafafi, J. P. LaFemina, and J. L. Nauss, "The Electronic Structure and Conformation of Polymers from Cluster Molecular Orbital and Molecular Mechanics Calculations: Polyimide," *J. Am. Chem. Soc.* (in press).
- J. P. LaFemina, "Electronic Band Structure of Graphite-Boron Nitride Alloys," *J. Phys. Chem.* **94**, 4346 (1990).
- J. P. LaFemina, "Hydrogen Atoms on Graphite: Effect of Interlayer Interactions on Chemisorption Pattern Stability," *Int. J. Quant. Chem.* (in press).
- J. P. LaFemina and G. Arjavalingam, "Photophysics of Poly(ethylene terephthalate): Ultraviolet Absorption and Emission," *J. Phys. Chem.* (in press).
- J. P. LaFemina and C. B. Duke, "Dependence of Oxide Cleavage Surface Structure on Crystal Structure and Local Chemical Bonding," *J. Vac. Sci. Tech.* (in press).
- J. P. LaFemina, C. B. Duke, and C. Mailhot, "New Surface Atomic Structures for III-V(110)-p(1x1)-Sb(1ML): Chemical Bonding and Electronic Structure," in *Atomic Scale Calculations of Structure in Materials*, M. A. Schluter and M. S. Daw, eds., Materials Research Society, Pittsburgh, 1990, pp. 41-46.
- J. P. LaFemina, C. B. Duke, and C. Mailhot, "New Surface Structures for Column V Overlayers on the (110) Surface of III-V Compound Semiconductors," *J. Vac. Sci. Tech.* **B8**, 888 (1990).
- J. P. LaFemina, C. B. Duke, and W. Rettig, "Molecular Conformations from Ultraviolet Photoelectron Spectra: Substituted Anilines," *J. Chem. Phys.* (in press).
- J. Lee, G. R. Holtom, and D. J. O'Kane, "Picosecond Resolution Study of Intramolecular Energy Transfer in Lumazine Protein," SPIE Proceedings **1204**, in *Time-Resolved Laser Spectroscopy in Biochemistry II*, 1990, p. 581.
- D. L. Lessor and C. B. Duke, "Analysis of the Differences Between Low-Energy Electron and Positron Diffraction: the Ion Core Potential," *Surf. Sci.* **81**, 225 (1990).
- D. L. Lessor, C. B. Duke, K. F. Canter, P. H. Lippel, G. R. Brandes, T. N. Horsky, and A. P. Mills, "Low-Energy Positron Diffraction on Cu(111)," *J. Vac. Sci. Tech.* (in press).
- R. J. Lipert and S. D. Colson, *J. Phys. Chem.* **93**, 3801 (1989).
- J. A. Loo, C. G. Edmonds, and R. D. Smith, "Primary Sequence Information from Electrospray Ionization Tandem Mass Spectrometry of Intact Proteins," *Science* **248**, 201-204 (1990).
- J. A. Loo, C. G. Edmonds, R. D. Smith, M. P. Lacey, and T. A. Keough, "Comparison of Electrospray Ionization and Plasma Desorption Mass Spectra of Peptides and Proteins," *Biomed. & Environ. Mass Spectrom.* **19**, 286-294 (1990).
- J. A. Loo, C. G. Edmonds, H. R. Udseth, R. R. Ogorzalek-Loo, and R. D. Smith, "Electrospray Ionization Mass Spectrometry and Tandem Mass Spectrometry of Large Biomolecules," *Experimental Mass Spectrometry* (in press).

- J. A. Loo, C. G. Edmonds, H. R. Udseth, and R. D. Smith, "Collisional Activation and Dissociation of Large Multiply Charged Proteins Produced by Electrospray Ionization," *Analytica Chimica Acta*. (in press).
- J. A. Loo, C. G. Edmonds, H. R. Udseth, and R. D. Smith, "Effect of Reducing Disulfide Containing Proteins on Electrospray Ionization Mass Spectra," *Anal. Chem.* **62**, 693-698 (1990).
- S. Lunell, D. Feller, and E. R. Davidson, "Configuration Interaction Calculations on the Propane Radical," *Theoret. Chim. Acta* **77**, 111 (1990).
- G. C. Lynch, R. Steckler, D. W. Schwenke, A.J.C. Varandas, D. G. Truhlar, and B. C. Garrett, "Use of Scaled External Correlation, a Double Many-Body Expansion, and Variational Transition State Theory to Calibrate a Potential Energy Surface for FH_2 ," *J. Chem. Phys.* (in press).
- E. P. Marsh, T. L. Gilton, W. Meier, M. A. Schneider, and J. P. Cowin, *Phys. Rev. Lett.* **61**, 2535 (1988).
- E. P. Marsh, L. Prat, T. L. Gilton, and J. P. Cowin, "Notch Filter and Fast Current Amplifier for Use with Time-Resolved Quadrupole Mass Spectroscopy," *Rev. Sci. Instrum.* **60**, 3070 (1989).
- E. P. Marsh, F. L. Tabares, M. R. Schneider, T. L. Gilton, W. Meier, and J. P. Cowin, "Perturbations, Inhibitions, Promotion of UV Surface Photochemistry of CH_3Br on $\text{Br}/\text{Ni(III)}$," *J. Chem. Phys.* (1989).
- E. P. Marsh, F. L. Tabares, M. R. Schneider, T. L. Gilton, W. Meier, and J. P. Cowin, *J. Chem. Phys.* **92**, 2004 (1990).
- P. F. McMillian and A. C. Hess, "Ab Initio Valence Force Field Calculations for α -Quartz," *Phys. Chem. Minerals* **17**, 97-107 (1990).
- R. J. Miller and B. A. Bushaw, "Continuous Wave-Continuous Wave Molecular Double Resonance Spectroscopy: Lifetimes and Term Energies of Individual Rovibronic Levels of the $(4p\pi)K^2\Pi(v=2)$ Rydberg State of Nitric Oxide," *J. Chem. Phys.* **92**, 3245-7 (1990).
- R. J. Miller, W. L. Glab, and B. A. Bushaw, "Two-Photon Spectroscopy at Ultrahigh Resolution: Fine Structure and Hyperfine Structure of the $(3s\sigma)4^2\Sigma^+(v=1, N=3)$ Rydberg State of NO ," *J. Chem. Phys.* **91**, 3277 (1989).
- R. J. Miller, L. Li, Y. Wang, W. A. Chupka, and S. D. Colson, "Multiphoton Ionization Studies of NO : Spontaneous Decay Channels in the $(4p\pi)K^2\Pi(v=2)$ Rydberg State," *J. Chem. Phys.* **90**, 754-61 (1989).
- J. A. Nichols, R. A. Kendall, S. Cole, and J. Simons, "Theoretical Study of Anion-Molecule Interactions: $\text{H}(\text{HF}) - (\text{H}_2)\text{F}^+$," *J. Phys. Chem.* (in press).
- R. L. Ornstein, "C-H...X Hydrogen-Bonded Pseudo-Watson-Crick Base Pairing With 7-Deazanebularin and Canonical Bases in DNA and RNA," *Prog. Clin. Biol. Res.* **289** (Comput.-Assisted Model. Recept.-Ligand Interact.), 131-142 (1989).
- R. L. Ornstein, "Using Molecular Dynamics Simulations on Crambin to Evaluate the Suitability of Different Continuum Dielectric Models for Protein Simulations," *J. Biomolecular Structure & Dynamics* **7**, 1019-1041 (1990).
- S. Papp, J. M. Vanderkooi, C. S. Owen, G. R. Holtom, and C. M. Phillips, "Reactions of Excited Triplet States of Metal Substituted Myoglobin with Dioxxygen and Quinone," *Biophys. J.* **58**, 177 (1990).
- L. K. Randeniya, X. K. Zeng, R. S. Smith, and M. A. Smith, "The Temperature Dependence of Thermolecular Association Reactions $\text{N}_2^+ + 2\text{N}_2 \rightarrow \text{N}_4^+ + \text{N}_2$ and $\text{O}_2^+ + 2\text{O}_2 \rightarrow \text{O}_4^+ + \text{O}_2$ Occurring in Free Jet Expansions Below 20K," *J. Phys. Chem.* **93**, 9031 (1989).

- D. Ray, N. E. Levinger, J. M. Papanikolas, and W. C. Lineberger, *J. Chem. Phys.* **91**, 6533 (1989).
- S. W. Sharpe, Y. P. Zeng, C. Wittig, and R. A. Beaudet, "Infrared Absorption Spectroscopy of the CO₂-HX Complexes Using the CO₂ (ν_3) Chromophore: CO₂HF(DF) and CO₂HCl(DCl) Linear and CO₂HBr Bent Equilibrium Geometries," *J. Chem. Phys.* **92**, 943 (1990).
- R. D. Smith and C. J. Barinaga, "Internal Energy Effects in the Collision Induced Dissociation of Large Biopolymer Molecular Ions Produced by Electrospray Ionization: Tandem Mass Spectrometry of Cytochrome c," *Rapid Commun. Mass Spectrom.* **4**, 54-57 (1990).
- R. D. Smith, S. M. Fields, J. A. Loo, C. J. Barinaga, H. R. Udseth, and C. G. Edmonds, "Capillary Isotachopheresis with UV and Tandem Mass Spectrometric Detection for Peptides and Proteins," *Electrophoresis* **11**, 709-717 (1990).
- R. D. Smith, J. A. Loo, C. J. Barinaga, C. G. Edmonds, and H. R. Udseth, "Collisional Activation and Collision-Activated Dissociation of Large Multiply Charged Polypeptides and Proteins Produced by Electrospray Ionization," *J. Am. Soc. Mass Spectrom.* **1**, 53-62 (1990).
- R. D. Smith, J. A. Loo, C. G. Edmonds, C. J. Barinaga, and H. R. Udseth, "New Developments in Biochemical Mass Spectrometry: Electrospray Ionization," *Anal. Chem.* **62**, 882-899 (1990).
- R. D. Smith, J. A. Loo, C. G. Edmonds, C. J. Barinaga, and H. R. Udseth, "Sensitivity Considerations for Large Molecule Detection by Capillary Electrophoresis-Electrospray Ionization Mass Spectrometry," *J. Chromatography* **516**, 157-165 (1990).
- T. S. Tenforde (ed.), *Proceedings of the Workshop on High-Field NMR and Biological Applications*, Pacific Northwest Laboratory, PNL-SA-18016 (CONF-8909305), Richland, Washington, 1990 (workshop held on September 8-9, 1989).
- J. M. Zachara, C. E. Cowen, and C. T. Rusch, "The Surface Exchange of Divalent Metallic Cations on Calcite," *Geochim. Cosm. Acta.* (in press).
- Y. P. Zeng, S. W. Sharpe, D. Reifschneider, C. Wittig, and R. A. Beaudet, "Infrared Absorption Spectroscopy of Gas Phase N₂O-HX (H = F, Cl, Br) Weakly-Bonded Complexes Using the N₂O (ν_3) Chromophore," *J. Chem. Phys.* **93**, 183 (1990).

Manuscripts Not Yet Published

M. B. Bass, M. D. Paulsen, and R. L. Ornstein, "Rotational Mobility of Norcamphor in Cytochrome P450cam by a 200 Picosecond Molecular Dynamics Simulation" (in preparation).

K. M. Beck, Cheng-Chi Chuang, and M. I. Lester, "Single-Photon Laser-Induced Fluorescence Spectra of Supersonic Jet-Cooled CO (B-X)" (in preparation)

S. N. Beck, E. A. McCullough, and D. Feller, "*Ab Initio* Calculations of the ^{13}C Magnetic Hyperfine Parameters in (C_2^+) Using Numerical and Gaussian Basis Set Methods" (submitted).

J. G. Boyle, L. D. Pfefferle, E. E. Gulcicek, and S. D. Colson, "Laser-Driven Electron Ionization for a VUV Photoionization Time-Of-Flight Mass Spectrometer," *Rev. Sci. Instrum.* (submitted).

D. M. Chipman, I. Carmichael, and D. Feller, "Molecular Orbital Studies of Hyperfine Coupling Constants in the H_2CN and $\text{H}(\text{HO})\text{CN}$ Radicals" (submitted).

J. Fidy, G. R. Holtom, K.-G. Paul, and J. M. Vanderkooi, "The Binding of Naphthohydroxamic Acid to Horseradish Peroxidase Monitored by Zn-Mesoporphyrin Fluorescence Line Narrowing" (submitted).

D. Gauyacq, A. L. Roche, M. Seaver, S. D. Colson, and W. A. Chupka, "s and d Rydberg Complexes of NO Probed by Double Resonance Multiphoton Ionization in the Region $N^*=5$ to $n^*=25$: Multichannel Quantum Defect Analysis II," *Mol. Phys.* (accepted).

T. J. Godin, J. P. LaFemina, and C. B. Duke, "Dynamical Strain at Semiconductor Interfaces: Structure and Surface Phonons of $\text{GaAs}(110)\text{-p}(1\times1)\text{-Sb}$," *J. Vac. Sci. Tech.* (submitted).

E. E. Gulcicek, S. D. Colson, and L. D. Pfefferle (in preparation).

S. G. Hansen, G. Luckman, G. C. Nieman, and S. D. Colson, "Heterogeneous Processes in CF_4/O_2 Plasmas Probed Using Laser Induced Fluorescence of CF_2 ," *J. Appl. Phys.* (accepted).

R. J. Harrison and R. A. Kendall, "A Parallel Version of ARGOS: A Distributed Memory Model for Shared Memory UNIX Computers," *Theoret. Chim. Acta* (accepted).

R. J. Harrison, R. L. Shepard, and R. A. Kendall, "*Ab Initio* Quantum Chemistry in Parallel - Portable Tools and Applications" (in preparation).

A. C. Hess and T. H. Dunning, "*Ab Initio* Hartree-Fock Investigations of the Clay Mineral Kaolinite" (in preparation).

A. C. Hess and C. B. Duke, "Surface Induced Modifications of Dynamical Matrix Elements and Phonon Spectra by Tight-Binding Total Energy Models: Formalism and Application to One Dimensional Systems," *Phys. Rev. B* (submitted).

A. C. Hess, G. K. Schenter, J. P. LaFemina, and C. B. Duke, "Higher Order Analytic Derivatives of Tight Binding Basis Functions" (in preparation).

A. C. Hess and M. R. Thompson, "*Ab Initio* Hartree-Fock Calculations of Sodalite Using Periodic Boundary Conditions" (in preparation).

G. R. Holtom, "Laser Testing and Diagnostics—What Are the Beams Really Like?," *Laser Focus World* (in preparation).

- R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, "Electron Affinities of the First Row Atoms, Revisited" (in preparation).
- R. J. Littlefield and K. J. Maschhoff, "Distributed Solution of Dense Eigensystems: the Blocked Factored Jacobi Method," *J. Parallel and Distributed Computing* (submitted).
- R. J. Miller and B. A. Bushaw, "Doppler-Free Two-Photon Fluorescence Excitation Spectroscopy of the $A+X(1,0)$ Band of Nitric Oxide: Rotational Constants and the Fine Structure Parameter of the $(3s\sigma)4\ ^2\Sigma^+(v=1)$ Rydberg State of $^{14}\text{N}^{16}\text{O}$," *J. Mol. Spectrosc.* (in preparation).
- R. J. Miller and B. A. Bushaw, "On the Structural and Dynamical Properties of the $(4p\pi)K\ ^2\Pi(v=2)$ and the $(3d\delta)F\ ^2\Delta(v=3)$ Rydberg States of $^{14}\text{N}^{16}\text{O}$," *J. Chem. Phys.* (in preparation).
- R. J. Miller and W. L. Glab, "Multiphoton Ionization Studies of Nitric Oxide: The Rotational Spectrum of the $(3d\delta)F\ ^2\Delta(v=3)$ Rydberg State of $^{14}\text{N}^{16}\text{O}$," *J. Chem. Phys.* (in preparation).
- G. A. Natanson, B. C. Garrett, T. N. Truong, T. Joseph, and D. G. Truhlar, "The Definition of Reaction Coordinate for Reaction-Path Dynamics," *J. Chem. Phys.* (submitted).
- R. L. Ornstein, "Molecular Dynamics Simulations of the Hydrophilic Neurotoxin Protein Erabutoxin B: Evaluation of Different Dielectric and Hydrogen Atom Models" (submitted).
- M. D. Paulsen and R. L. Ornstein, "Molecular Dynamics Simulation of Camphor-Bound Cytochrome P450cam" (submitted).
- M. D. Paulsen and R. L. Ornstein, "Analysis of Active Site Motions from a 175 Picosecond Molecular Dynamics Simulation of Cytochrome P450cam" (in preparation).
- Report of the MSRC Conference on Graphical User Interfaces in Computational Chemistry* (in preparation).
- G. K. Schenter and C. B. Duke, "The Photoinduced Twisting Dynamics of Dimethyl-Aminobenzonitrile in Polar Solvents," *Chem. Phys. Lett.* (submitted).
- G. K. Schenter and J. P. LaFemina, "III-V Compound Semiconductor Phonon Spectra from Tight-Binding Molecular Dynamics Simulations," *Phys. Rev. B* (in preparation).
- M. R. Schneider, C. P. Dehnhostel, T. L. Gilton, and J. P. Cowin, "Photoelectron Induced Surface Chemistry: Methyl Chloride on GaAs(100)," *J. Appl. Phys.* (submitted).
- S. W. Sharpe, D. Reifschneider, C. Wittig, and R. A. Beaudet, "Infrared Absorption Spectroscopy of the $\text{CO}_2\text{-Ar}$ Complex in the 2376 cm^{-1} Region: Determination of the ν_5 Intermolecular Bending Frequency," *J. Chem. Phys.* (accepted).
- T. S. Tenforde (ed.), *Proceedings of the Workshop on the Development of a Gigahertz NMR Spectrometer* (Seattle, Washington, March 8, 1990), Pacific Northwest Laboratory, Richland, Washington (in preparation).
- Y. Thiel, V. A. Walters, K. B. Wiberg, and S. D. Colson, "High-Resolution Infrared Analysis of ^{17}O Band of Pyridine," *Int. J. Quant. Chem.* (accepted).
- V. A. Walters, C. M. Hadad, Y. Thiel, S. D. Colson, K. B. Wiberg, P. M. Johnson, and J. Foresman, "Assignment of the A State in Bicyclobutane—The Multiphoton Ionization Spectrum, and Calculations of Transition Energies," *Am. Chem. Soc.* (accepted).

G. Wolf, P. F. McMillian, and A. C. Hess, "Phase Fields of KO_2 at Diamond Anvil Pressures," *Phys. Chem. Solids* (submitted).

M. A. Zhenyi, S. C. Lanford, J. T. Dickinson, D. R. Baer, and M. H. Engelhard, "Fractal Character of Crack Propagation in Epoxy and Epoxy Composites as Revealed by Photon Emission During Fracture," *J. Mat. Res.* (submitted).

Presentations

K. J. Adams, "Upgrading User Interface to Computational Chemistry Codes," presented at the TAE Conference, Houston, Texas, June 5, 1990.

K. J. Adams and J. J. Thomas, "PNL Experience Using TAE+ - A Rapid Prototyping Tool," presented at the SIGCHI Conference, Seattle, Washington, April 6, 1990.

D. R. Baer, D. L. Blanchard, M. H. Engelhard, and J. M. Zachara, "The Interaction of Water and Mn with Surfaces of CaCO_3 : an XPS Study," poster at Gordon Research Conference on Fundamental of Interaction of Water with Surfaces, July 1990.

D. R. Baer, D. L. Blanchard, M. H. Engelhard, and J. M. Zachara, "MSRC Materials and Interface Program and Surface Studies of CaCO_3 ," presented at 12th Northwest Meeting on Condensed Matter Physics, Seattle, Washington, April 1990.

D. R. Baer, D. L. Blanchard, M. H. Engelhard, and J. M. Zachara, "Surface Studies of CaCO_3 Relevant to Groundwater Contamination," presented at the Pacific Coast Regional Meeting of the American Ceramics Society, Seattle, Washington, October 1990.

D. R. Baer, D. L. Blanchard, M. H. Engelhard, and J. M. Zachara, "XPS Measurements of the Surface Chemistry of CaCO_3 ," presented at Applied Surface Analysis Symposium, Albuquerque, New Mexico, April 1990.

D. R. Baer, D. L. Blanchard, and J. M. Zachara, "Calcium Carbonate Surface Chemistry," poster presentation, Fundamental Interactions of Water with Surfaces Gordon Conference, July 1990.

M. B. Bass and R. L. Ornstein, "Molecular Dynamics Simulations of Cytochrome P450cam with an Alternate Substrate, Norcamphor," presented at the symposium on *Converging Approaches in Computational Biology*, SUNY/Albany, Albany, New York, September 13-15, 1990.

M. B. Bass, M. D. Paulsen, and R. L. Ornstein, "Comparison of Implicit and Explicit Solvent Molecular Dynamics Simulations for Avian Pancreatic Polypeptide Hormone," presented at the AAAS Annual Meeting, New Orleans, Louisiana, February 15-20, 1990.

K. M. Beck, "Photodissociation of Ar-X Complexes by Novel Non-Linear Techniques," presented at the Naval Research Laboratories, Chemistry Division, Washington, D.C., July 16, 1990.

K. M. Beck, "Single-Photon Laser-Induced Fluorescence Excitation Spectra of Supersonic-Jet Cooled CO (B-X)," presented at the University of Central Florida, Department of Chemistry, Orlando, Florida, March 16, 1990.

K. M. Beck, "Symposium on Intermolecular Potentials: Spectroscopic, Theoretical, and Dynamical Probes," presented at the ACS National Convention, Washington, D.C., August 1990.

K. M. Beck, "Vibrational Overtone Spectroscopy of OH-Ar Complexes," presented at the Princeton University, Interdisciplinary Science Seminar, Princeton, New Jersey, November 30, 1989.

R. S. Blake, "Chemical Dynamics at the Complex Interface," presented at Washington State University, Pullman, Washington, November 27, 1990.

R. S. Blake, "From Bytes to Backplanes: Principles, Methods and Technology in Laboratory Data Acquisition, Control and Analysis," short course presented at Scientific Computing and Automation/Industrial Data Acquisition and Control Conference and Exposition, Philadelphia, Pennsylvania, September 17-20, 1990.

- R. S. Blake, "New Technologies in the Laboratory," presented at Computing and Automation/Industrial Data Acquisition and Control Conference and Exposition, Philadelphia, Pennsylvania, September 17-20, 1990.
- R. S. Blake, "Prototypes for Laboratory Computation and Control at the Pacific Northwest Laboratory," presented at Naval Research Laboratories, Washington, D.C., February 23, 1990.
- R. S. Blake, "Prototypes for Laboratory Computation and Control at the Pacific Northwest Laboratory," presented at Schlumberger-Doll Research, Ridgefield, Connecticut, April 26, 1990.
- D. L. Blanchard and D. R. Baer, "Structure and Composition of the SnO_2 Surface," presented at the AVS Pacific Northwest Chapter Symposium, Vancouver, British Columbia, Canada, September 8, 1990.
- D. L. Blanchard, D. L. Lessor, J. P. LaFemina, D. R. Baer, W. K. Ford, and T. Guo, " $\text{MgO}(100)$ Studies by Modulated Beam Low Energy Electron Diffraction," presented at the AVS National Symposium, Toronto, Ontario, Canada, October 1990.
- B. A. Bushaw, "Structure and Dynamics from High Resolution Spectra of Small Molecules," presented at the Gordon Research Conference on Multiphoton Processes, New London, New Hampshire, June 11-15, 1990.
- S. D. Colson, presentations given on the general topic of hydrogen bonding in clusters at the following institutions: University of California, Riverside, California; University of Washington, Seattle, Washington; Washington State University, Pullman, Washington; University of Munich, Munich, West Germany; University of Ulm, Ulm, West Germany; and Centre National de la Recherche Scientifique, Orsay, France.
- J. P. Cowin, "Dynamical Processes in Surface Photochemistry," presented at the American Physical Society, Anaheim, California, March 12-15, 1990.
- J. P. Cowin, "Electron Transfers in Surface Photochemistry: Quenching and Promotion," presented at the American Chemical Society, Washington, D.C., August 26-31, 1990.
- J. P. Cowin, "Electron Transmission Through Water in UHV," poster presentation, Electrochemical Gordon Conference, Ventura, California, January 15-19, 1990.
- J. P. Cowin, "Femtosecond Photoelectron Chemistry at Surfaces: Transmission and Solvation," presented at the Kinetics at Surfaces Symposium, Irvine, California, October 21-24, 1990.
- J. P. Cowin, "Femtosecond Solvation Dynamics on Surfaces," presented at the Physics Department Colloquium, *Laser-Induced Electron Emission: Space Charge and Electron Acceleration*, Graduate Seminar, Washington State University, Pullman, Washington, October 30, 1990.
- J. P. Cowin, "Hot Electron Chemistry at Surfaces," presented at the Chemistry Department, University of California, San Diego, California, February 20, 1990.
- J. P. Cowin, "UHV Photoelectron Chemistry at Interfaces," presented at the International Conference on Photoinduced Charge Transfer, Rochester, New York, June 6-9, 1990.
- J. P. Cowin, presentation at the Cluster Workshop, Seattle, Washington, June 16-19, 1990.
- J. P. Cowin, presentation at the Combustion Dynamics Facility, Berkeley, California, April 5-7, 1990.
- T. H. Dunning, Jr., "Molecular Theory, Modeling and Simulation: Application to Research and Real-World Problems," presented at the Computational Chemistry Seminar, Idaho National Engineering Laboratory, Idaho Falls, Idaho, February 21, 1990.

T. H. Dunning, Jr., "Molecular Theory, Modeling and Simulation: Application to Research and Real-World Problems," presented at the University of Kentucky, Lexington, Kentucky, September 19, 1990.

T. H. Dunning, Jr., "Pathways for Chemical Reactions: A Window into the Heart of Chemistry," presented at the University of Washington, Seattle, Washington, October 4, 1989.

T. H. Dunning, Jr., "Potential Energy Surfaces and Reaction Dynamics," presented at the 1989 International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, December 17-22, 1989.

T. H. Dunning, Jr., "Reaction Path Analysis of Molecular Potential Energy Surfaces," presented at the Symposium on the Reaction Path in Chemistry, 199th American Chemical Society National Meeting, Boston, Massachusetts, April 22-27, 1990.

T. H. Dunning, Jr., "Theory, Modeling and Simulation: Application to Research and Real-World Problems," presented at the Chemical Physics Institute, University of Oregon, Eugene, Oregon.

T. H. Dunning, Jr., "Theory, Modeling and Simulation Program in the Molecular Science Research Center and Basis Sets for Correlated Calculations on Sulfur-Containing Compounds," presented at the Workshop on Methodology of the Evaluation of Integrals in LCAO Calculations, Argonne National Laboratory, Argonne, Illinois, August 23-25, 1990.

T. H. Dunning, Jr., "Theory, Modeling and Simulation Program in the Molecular Science Research Center," presented at the Regional American Chemical Society Meeting, University of Utah, Salt Lake City, Utah, June 13-15, 1990.

D. Feller, "*Ab Initio* Studies of Magnetic Hyperfine Properties of F_2^+ (C_2^+)," presented at the West Coast Theoretical Chemistry Conference, Salt Lake City, Utah, March 23, 1990.

B. C. Garrett, "The Direct Use of *Ab Initio* Electronic Structure Information in Variation Transition State Theory," presented at the NATO Advanced Studies Institute on Theoretical and Computational Models for Organic Chemistry, Porto Novo, Portugal, August 26-September 8, 1990.

B. C. Garrett, "Dynamics Calculations Based on *Ab Initio* Calculations of Reaction Path: Applications to $H_2 + NH_2 \rightarrow H + NH_3$ and $H_2 + CN \rightarrow H + HCN$," presented at the West Coast Theoretical Chemistry Conference, University of Utah, Salt Lake City, Utah, March 23-25, 1990.

B. C. Garrett, "Dynamics Calculations Based on Reaction Path Methods: Techniques and Applications," presented at the Symposium on the Reaction Path in Chemistry, 199th American Chemical Society National Meeting, Boston, Massachusetts, April 22-27, 1990.

B. C. Garrett, "Variational Transition State Theory for the Calculation of Reaction Rate Constants," presented at the NATO Advanced Studies Institute on Theoretical and Computational Models for Organic Chemistry, Porto Novo, Portugal, August 26-September 8, 1990.

B. C. Garrett, "Variational Transition State Theory Calculations of Rates of Reactions in the Gas Phase, at Interfaces, and in Condensed Phases," presented at Washington State University, Pullman, Washington, May 4, 1990.

A. C. Hess, "Periodic Hartree-Fock Calculations of the Clay Mineral Kaolinite," presented at *Ab Initio Treatment of Crystalline Systems: Hartree-Fock and Beyond*, European Center for Atomic and Molecular Calculations, Orsay, France, October 17-19, 1990.

A. C. Hess and C. B. Duke, "Analytical Investigations of Vibrational Properties Obtained From the Tight Binding Total Energy Model," presented at the American Physical Society, Anaheim, California, March 1990.

W. P. Hess, "Ion Imaging of Photofragments: The Photodissociation of CH_3Br , $\text{CH}_3\text{CH}_2\text{Br}$, and $\text{BrCH}_2\text{CH}_2\text{OH}$," presented at the University of Nevada, Las Vegas Physics Symposium, Las Vegas, Nevada, April 1990.

W. P. Hess, "The Photodissociation of $\text{BrCH}_2\text{CH}_2\text{OH}$ by Photofragment Imaging and Laser-Induced Fluorescence," presented at the University of Idaho Chemistry Symposium, Moscow, Idaho, March 1990.

W. P. Hess, "Photofragment Imaging: The Photodissociation of Bromomethane, Bromoethane, Bromoethanol," presented at the Fifth International Symposium on Resonance Ionization Spectroscopy and Its Applications, Varese, Italy, September 1990.

G. R. Holtom, "Artifacts and Diagnostics in Fast Fluorescence Measurements," presented at the SPIE Conference on *Time-Resolved Laser Spectroscopy in Biochemistry II*, Los Angeles, California, January 15, 1990.

R. A. Kendall, "*Ab Initio* Quantum Chemistry in Parallel - Portable Tools and Applications: A Parallel Version of ARGOS," presented at Argonne National Laboratory, Argonne, Illinois, August 1990.

R. A. Kendall, "The Molecular Science Research Center and the Environmental and Molecular Sciences Laboratory at Pacific Northwest Laboratory," presented at Indiana State University, Terre Haute, Indiana, August 1990.

R. A. Kendall and T. H. Dunning, Jr., "Electron Affinities of the First Row Atoms, Revisited," poster presentation at the West Coast Theoretical Chemistry Conference, University of Utah, Salt Lake City, Utah, March 23-25, 1990.

J. P. LaFemina, "Structure of Metal Overlayers on III-V Compound Semiconductors," presented at the Twelfth Northwest Meeting on Condensed Matter Physics, University of Washington, Seattle, Washington, April 7, 1990.

J. P. LaFemina and C. B. Duke, "Topology and Surface Reconstructions in Oxides," presented at the American Vacuum Society Pacific Northwest Vancouver Symposium, Vancouver, British Columbia, September 8, 1990.

J. P. LaFemina, C. B. Duke, and C. Mailhot, "Atomic Structure of $\text{p}(1\times 1)$ -Sb Overlayers on the (110) Surface of III-V Compound Semiconductors: A Question of Size?," presented at the Seventeenth Annual Conference on the Physics and Chemistry of Semiconductor Interfaces, Tampa, Florida, January 31-February 2, 1990.

J. P. LaFemina, C. B. Duke, and C. Mailhot, "New Surface Atomic Structures for III-V(110)- $\text{p}(1\times 1)$ -Sb(1ML): Chemical Bonding and Electronic Structure," presented at the 1990 Spring Meeting of the Materials Research Society, San Francisco, California, April 16-21, 1990.

J. P. LaFemina, C. B. Duke, and C. Mailhot, "Surface Atomic and Electronic Structure of Column V Overlayers on III-V(110) Surfaces," presented at the March 1990 Meeting of the American Physical Society, Anaheim, California, March 12-16, 1990.

J. P. LaFemina, S. A. Kafafi, and J. L. Nauss, "Atomic and Electronic Structure of Polyimide," presented at the March 1990 Meeting of the American Physical Society, Anaheim, California, March 12-16, 1990.

R. J. Miller, "High Resolution Rydberg State Spectroscopy of NO ," presented at the Chemical Physics Section, Oak Ridge National Laboratory, Oak Ridge, Tennessee, November 8, 1989.

R. J. Miller, "High Resolution Studies of Nitric Oxide: Structure and Dynamics of Rydberg States," presented at Max-Planck-Institut für Strömungsforschung, Göttingen, Germany, March 22, 1990.

- R. L. Ornstein, "Molecular Dynamics Simulations of Cytochrome P450cam," presented at the Regional ACS Meeting, University of Utah, Salt Lake City, Utah, June 13-15, 1990.
- R. L. Ornstein, "Molecular Dynamics Simulations: Protein Validation Studies and Cytochrome P450cam Applications," presented at the Midwest Biotechnology Symposium, University of Minnesota, St. Paul, Minnesota, May 21-23, 1990.
- R. L. Ornstein, "Molecular Dynamics Simulations: Validation Studies and Simulations of Cytochrome P450cam," presented at the University of Oregon, Institute of Molecular Biology & Institute of Materials, Eugene, Oregon, October 22-23, 1990.
- R. L. Ornstein, "Molecular Dynamics Simulations: Validation Studies and Simulations of Cytochrome P450cam," presented at the University of Washington, Seattle, Washington, July 9, 1990.
- R. L. Ornstein, "Molecular Dynamics Simulations: Validation Studies and Simulations of Cytochrome P450cam," presented at the Washington State University, Pullman, Washington, April 25, 1990.
- R. L. Ornstein, "Molecular Issues in Environmental Bioremediation," presented at the *Workshop on Molecular Science Computing Facility*, Richland, Washington, February 7, 1990.
- R. L. Ornstein, "Overview and Update on Biomacromolecular Simulations at the MSRC," presented at the University of British Columbia, Vancouver, British Columbia, Canada, May 17, 1990.
- R. L. Ornstein, "Protein Dynamics Simulations: Validation and Applications," presented at the 3rd INEL Computer Conference, Idaho Falls, Idaho, October 1989.
- R. L. Ornstein, "Protein Dynamics Simulations: Validation and Applications," presented at the Montana State University, Bozeman, Montana, October 25, 1989.
- R. L. Ornstein and M. B. Bass, "Molecular Dynamics Simulations of Cytochrome P450cam With an Alternate Substrate, Norcamphor," presented at the ACS North Carolina Annual Symposium, *Challenges in Computational Chemistry*, University of North Carolina, Raleigh, North Carolina, September 14-15, 1990.
- R. L. Ornstein and M. B. Bass, "Molecular Dynamics Simulations: Validation Studies and Simulations of Cytochrome P450cam," presented at the Roswell Park Memorial Institute, Buffalo, New York, May 14, 1990.
- R. L. Ornstein, M. D. Paulsen, and M. B. Bass, "Molecular Dynamics Simulations of the Biodegradative Enzyme Cytochrome P450cam," presented at the Conference on Biodegradation of Hazardous Wastes, sponsored by NIEHS, Utah State University, Logan, Utah, April 9-10, 1990.
- R. L. Ornstein, M. D. Paulsen, and M. B. Bass, "Molecular Dynamics Simulations of Cytochrome P450cam," presented at the Regional ACS Meeting, University of Utah, Salt Lake City, Utah, June 13-15, 1990.
- R. L. Ornstein, M. D. Paulsen, and M. B. Bass, "Molecular Dynamics Simulations: Protein Validation Studies and Cytochrome P450cam Applications," presented at the Midwest Biotechnology Symposium, University of Minnesota, St. Paul, Minnesota, May 21-23, 1990.
- M. D. Paulsen, "Molecular Dynamics Simulations of Cytochrome P450cam," presented at the National Institute of Standards & Technology, Polymers Division, Gaithersburg, Maryland, April 3, 1990.
- M. D. Paulsen, M. B. Bass, and R. L. Ornstein, "Molecular Dynamics Simulations of Cytochrome P450cam," presented at the AAAS Annual Meeting, New Orleans, Louisiana, February 15-20, 1990.

M. D. Paulsen and R. L. Ornstein, "Molecular Dynamics Simulations of Cytochrome P450cam," presented at the 7th International Symposium on Microsomes & Drug Oxidations, Karolinska Institutet, Stockholm, Sweden, June 25-29, 1990.

M. D. Paulsen and R. L. Ornstein, "Molecular Dynamics Simulations of Human EGF," presented at the Gordon Research Conference on Proteins, Plymouth, New Hampshire, June 1989.

D. Ray, "Spectroscopy and Dynamics of Cluster Ions," Cluster Workshop, Telluride Summer Research Center, Telluride, Colorado, July 2-6, 1990.

D. Ray, "Spectroscopy and Dynamics of Cluster Ions," presented at the Physical Chemistry Colloquium, Department of Chemistry, Oregon State University, Eugene, Oregon, October 10, 1990.

D. Ray, "Ultrafast Time-Resolved Dynamics in Cluster Ions," presented at the Fifth International Symposium on Small Particles and Inorganic Clusters, Konstanz, West Germany, September 10-14, 1990.

D. Ray, "Ultrafast Time-Resolved Dynamics in Cluster Ions," presented at the Sixth Interdisciplinary Laser Science Conference, Minneapolis, Minnesota, September 1990.

G. K. Schenter, "Theory of Twisted Intramolecular Charge Transfer," presented at the Washington State University, Pullman, Washington, September 17, 1990.

G. K. Schenter and C. B. Duke, "Dynamics of Twisted-Intramolecular Charge Transfer in Dimethylaminobenzonitrile," presented at the 199th American Chemical Society National Meeting, Boston, Massachusetts, April 22-27, 1990.

G. K. Schenter and C. B. Duke, "Dynamics of Twisted-Intramolecular Charge Transfer in Dimethylaminobenzonitrile," presented at the West Coast Theoretical Chemistry Conference, University of Utah, Salt Lake City, Utah, March 23-25, 1990.

G. K. Schenter and C. B. Duke, "The Theory of Photoinduced Twisting Dynamics in Polar Solvents: Application to Dimethylaminobenzonitrile in Propanol," presented at the 7th American Conference on Theoretical Chemistry, San Diego, California, July 29-August 3, 1990.

S. W. Sharpe, "Spectroscopy and Dynamics of a Few Weakly Bonded Complexes: A High-Resolution Infrared Diode Laser Technique," presented at the University of Washington, Seattle, Washington, November 14, 1990.

J. J. Thomas, "Designing Complex Information Systems," presented at MITRE, Washington, D.C., November 16, 1989.

J. J. Thomas, "Information Science: Challenges and Opportunities," presented at the University of Puget Sound, Tacoma, Washington, November 30, 1989.

J. J. Thomas, "User Interface Tools to Bridge Science and Computing Into the Future," presented at IBM-Watson Research Laboratory, New York, New York, May 7, 1990.

J. J. Thomas, "User Interface Tools to Bridge Science and Computing Into the Future," presented at User Interface Software & Technology Conventions, Williamsburg, Virginia, November 13, 1989.

J. J. Thomas, "Visualization Systems: Experience, Needs, and Techniques," presented at the Software Psychology Society, Washington, D.C., October 13, 1989.

J. J. Thomas, "Visualization: A View of Science," presented at the San Diego Supercomputing Center, San Diego, California, January 29, 1990.

J. J. Thomas, E. W. Pearson, T. H. Dunning, J. W. Brothers, and J. J. Fallon, "User Interface Tools to Bridge Science and Computing Into the Future," presented at Digital Equipment Company, Marlborough, Minnesota, April 24, 1990.

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: Atmospheric Clusters
Organization: University of Washington
MSRC Contact: S. W. Sharpe

Topic: Atomic Resolution Probes of Surface Chemistry
Organization: IBM
MSRC Contact: J. P. Cowin

Topic: Atomic-Scale Models of Heteroepitaxy
Organization: Montana State University
MSRC Contact: J. P. LaFemina

Topic: Comparison Between Fully Numerical and Basis Set Approaches to *ab initio* Quantum Chemistry Determinations of Properties
Organization: Utah State University
MSRC Contact: D. F. Feller

Topic: Defect Structures in Oxides
Organizations: University of Oregon and Pennsylvania State University
MSRC Contact: J. P. LaFemina

Topic: Direct Participation of Solvent Molecules in Chemical Reactions
Organizations: Sandia National Laboratory and University of California-Berkeley
MSRC Contact: B. C. Garrett

Topic: Excited-State Proton Transfer
Organization: University of California-Berkeley
MSRC Contact: J. P. Cowin

Topic: Experimental and Theoretical Studies of the Hyperfine Properties of Small Molecules
Organization: Furman University
MSRC Contact: D. F. Feller

Topic: Hydrogen Bonding - Theory and Experiment
Organization: University of Washington
MSRC Contact: S. D. Colson

Topic: Incorporating Continuum Dielectric Solvation Effects in Variational Transition-State Theory
Organization: University of Minnesota
MSRC Contact: B. C. Garrett

Topic: Investigation of the Twisted Intramolecular Charge Transfer Mechanism in Dimethylaminobenzonitrile
Organization: Xerox Webster Research Center
MSRC Contact: G. K. Schenter

Topic: Low-Energy Electron and Positron Diffraction Determinations of Compound Semiconductor and Metal Surfaces
Organizations: Brandeis University and Xerox Webster Research Center
MSRC Contact: J. P. LaFemina

Topic: Low-Energy Electron Diffraction Determination of Oxide Surface Structures
Organization: University of Texas at Austin
MSRC Contact: J. P. LaFemina

Topic: Methane Conversion
Organization: AMOCO
MSRC Contact: S. D. Colson

Topic: Molecular Dynamics Program Development
Organizations: Roswell Park Memorial Institute and State University of New York-Buffalo
MSRC Contact: R. L. Ornstein

Topic: Molecular Dynamics - Theory and Experiment
Organization: University of Washington
MSRC Contact: M. O. Trulson

Topic: Molecular Models of Dielectric Polymers
Organizations: Johns Hopkins University, St. Mary's College, and University of Utah
MSRC Contact: J. P. LaFemina

Topic: NMR of Cytochrome Proteins
Organization: Washington State University
MSRC Contact: R. L. Ornstein

Topic: Reactions on High-Energy Surfaces
Organization: University of Pittsburgh
MSRC Contact: S. D. Colson

Topic: Real-Time Measurements of Surface Reaction Dynamics
Organization: University of California-San Diego
MSRC Contact: R. S. Blake

Topic: Sequence Attributes Analysis of Protein Structure
Organization: Washington State University
MSRC Contact: R. L. Ornstein

Topic: Site-Directed Mutagenesis and Biochemistry of Cytochrome P450CAM
Organization: University of Illinois-Urbana
MSRC Contact: R. L. Ornstein

Topic: Surface Atomic and Electronic Structure of Oxides and Carbonates
Organization: Xerox Webster Research Center
MSRC Contact: J. P. LaFemina

Topic: Synthesis and Design of Artificial Cytochrome P450s/NMR of Structures
Organization: University of Washington
MSRC Contact: R. L. Ornstein

Topic: Synthetic Radical Sites on Surfaces
Organization: University of Colorado
MSRC Contact: J. P. Cowin

Topic: Theoretical Studies of One Electron Properties
Organization: University of Amsterdam
MSRC Contact: D. F. Feller

Topic: Theoretical Studies of Transition Metal Compounds Using the Multireference Averaged Couple Pair Functional Method
Organization: Harvey Mudd College
MSRC Contact: D. F. Feller

Topic: Variational Transition-State Theory - Developments for Gas Phase Reactions
Organization: University of Minnesota
MSRC Contact: B. C. Garrett

Topic: X-Ray Crystal Structure Determination of Redesigned P450 Cam Mutant-Contaminant
Organizations: University of Maryland and CARB
MSRC Contact: R. L. Ornstein

Colloquia Speakers During FY 1990

Dr. Ian M. Armitage, Yale University School of Medicine
 Dr. Philip N. Borer, Syracuse University
 Dr. Richard W. Briggs, University of Florida
 Dr. Brian Chait, Rockefeller University
 Dr. Grzegorz M. Chalaskinski, University of Warsaw
 Dr. Dan Chipman, University of Notre Dame
 Dr. David Coker, Boston University
 Dr. Kelsey Cook, University of Tennessee
 Dr. Killian Dill, College of Science, Clemson University
 Dr. David A. Dixon, E.I. Du Pont de Nemours and Co. Inc.
 Dr. Michael Dupuis, IBM Corporation
 Dr. Dale Durand, University of Illinois
 Dr. James L. Erskine, University of Texas
 Ross Faneuf, Digital Equipment Corp.
 Dr. James A. Ferretti, National Institutes of Health
 Dr. Robert B. Gerber, University of California-Irvine
 Professor John T. Gerig, University of California-Santa Barbara
 Dr. Thomas Godin, University of Oregon
 Professor Wayne Goodman, Texas A&M University
 Dr. Edward R. Grant, Purdue University
 Dr. Roger Haydock, University of Oregon
 Professor A.J.C. Haymet, University of Utah
 Dr. Deborah Hix, Virginia Tech.
 Dr. Kendall N. Houk, University of California-Los Angeles
 Professor Neal Ivory, Washington State University
 Professor Hannes Jonsson, University of Washington
 Professor Scott Kahn, University of Illinois
 Dr. Michael A. Kennedy, University of California-San Diego
 Dr. Stephen D. Kevan, University of Oregon
 Dr. David H. Kitson, Biosym Technologies, Inc.
 Professor Dahn A. V. Kliner, Stanford University
 Dr. Peter P. Lambropoulos, University of Southern California

Dr. Christoph A. Lang, Stanford University
 Dr. W. Carl Lineberger, University of Colorado
 Dr. John P. Lowe, Pennsylvania State University
 Professor Douglas Magde, University of California-San Diego
 Dr. Maureen McCarthy, The Hebrew University
 Professor W. M. McClain, Wayne State University
 Dr. Carl F. Melius, Sandia National Laboratory
 Professor George Nemethy, Mt. Sinai School of Medicine
 Irene Newhouse, Space Power Institute, Auburn University
 Dr. Michael O'Keefe, Arizona State University
 Dr. Cedric Powell, National Institute of Standards and Technology
 Professor Ron Poshusta, Washington State University
 Dr. Thomas L. Poulos, University of Maryland
 Dr. Robert Powers, Purdue University
 Dr. Lawrence Pratt, Los Alamos National Laboratory
 Dr. Herschel Rabitz, Princeton University
 Dr. William Rogers, Sandia National Laboratories
 Professor David H. Russell, Texas A&M University
 Dr. James Satterlee, Washington State University
 Dr. Victor R. Saunders, Daresbury Laboratory
 Dr. George Schatz, Northwestern University
 Dr. Harrell Sellers, University of Illinois
 Dr. Randal B. Shirts, EG&G Idaho
 Professor John D. Simon, University of California-San Diego
 Dr. Arthur W. Sleight, Oregon State University
 Dr. Lloyd M. Smith, University of Wisconsin
 Dr. Brian D. Sykes, University of Alberta
 Dr. Andy Van Dam, Brown University
 Dr. Gregory A. Voth, University of Pennsylvania
 Dr. Philip R. Watson, Oregon State University
 Professor Ken Wiberg, Yale University
 Dr. James P. Yesinowski, Michigan State University
 Professor William Zoller, University of Washington

Technical Advisory Panel

Professor J. Gregory Dash
Department of Physics
University of Washington

Professor Mostafa El-Sayed
Department of Chemistry & Biochemistry
University of California-Los Angeles

Dr. Robert J. Fletterick
Biochemistry & Biophysics Department
University of California-San Francisco

Professor Hans Frauenfelder
Department of Physics
University of Illinois

Dr. Jeffrey Hay
Los Alamos National Laboratory

Professor Yuan T. Lee
Department of Chemistry
University of California-Berkeley

Dr. Brian W. Matthews
Institute of Molecular Biology
University of Oregon

Dr. Marvin Poutsma
Oak Ridge National Laboratory

Dr. John T. Yates, Jr., Director
Pittsburgh Surface Science Center
Department of Chemistry
University of Pittsburgh

Tours and Visitors During FY 1990

Universities

Emory University
Gonzaga University
Montana State University
North Carolina State University
Northwestern University
Ohio State University
Oregon Graduate Institute
Oregon State University
Oxford University
Rice University
St. Mary's College
Texas A&M University
University of California
University of Cincinnati
University of Florida
University of Idaho
University of Illinois
University of Kentucky
University of Minnesota
University of Oregon
University of Utah
University of Washington
University of Wisconsin, Madison
Washington State University
Yale University

Industry

Bell Laboratories
The Boeing Company
Chemical Industry Institute of Toxicology
Cray Research Inc.
E.I. DuPont de Nemours and Co., Inc.
Environmental Trade Association
IBM Research Laboratory
Massachusetts General Hospital
SUN Microsystems

International

Mitsubishi Corporation (Japan)
Pacific Rim/International Delegations
Power Reactor & Nuclear Field Development Corporation (Japan)

Other National Laboratories

Argonne National Laboratory
Brookhaven National Laboratory
Lawrence Berkeley Laboratory
Los Alamos National Laboratory
Sandia National Laboratory

Government

DOE, Budget Analysis Division
DOE, ECUT Thermal Science Program
DOE, Office of Conservation and Renewable Energy
U.S. Navy
U.S. Secretary of Energy

Legislative

Congressional Office of Technology Assessment
Senate Appropriations Committee
U.S. Presidential Science Advisor representative
U.S. Senate Appropriations Committee
Washington State Democrats

Appendix D

Acronyms and Abbreviations

Appendix D

Acronyms and Abbreviations

AFM - atomic force microscopy	(program)
amu - atomic mass unit	M - molar
CE - capillary electrophoresis	MHz - megahertz
CID - collision-induced dissociation	MIMD - multiple instruction-multiple data
cm - centimeter	min - minute
CSDRF - Cluster Structure and Dynamics Research Facility	mm - millimeter
CVT - canonical variational theory	MPa - megapascal
DMABN - dimethylaminobenzonitrile	MR-SDCI - multireference singles and doubles configuration interaction
DNA - deoxyribonucleic acid	MS - mass spectrometry
DNP - dynamic nuclear polarization	MSCF - Molecular Science Computing Facility
DOE - U.S. Department of Energy	MSRC - Molecular Science Research Center, Pacific Northwest Laboratory, Richland, Washington
EA - electron affinity	MW - molecular weight
ECLS - epitaxial continued layer structure	NBO - natural bond orbital (analysis)
EDS - Environmental Dynamics and Simulation (program)	NMR - nuclear magnetic resonance
EMSL - Environmental and Molecular Sciences Laboratory	NO - nitric oxide
EOCS - epitaxial overlapping structure	NORCUS - Northwest Colleges and Universities Association for Science
EOTS - epitaxial on top structure	ns - nanosecond
ESI - electrospray ionization	PES - potential energy surface
ESR - electron spin resonance	PNL - Pacific Northwest Laboratory
ESRC - Environmental Science Research Center, Pacific Northwest Laboratory, Richland, Washington	ppb - parts per billion
eV - electron volts	ps - picosecond
fmol - femtomole	QMMD - quantum-mechanical molecular dynamics
fs - femtosecond	RF - radio frequency
FY - fiscal year	RHEED - reflection high-energy electron diffraction
GHz - gigahertz	rms - root mean square
GLE - Generalized Langevin Equation	s - second
GUI - graphical user interface	S - siemens
GW - gigawatt	SCF - self-consistent field
Hz - hertz	SCSAG - small-curvature semiclassical adiabatic ground-state
IP - ionization potential	STM - scanning tunneling microscopy
IR - infrared	TBTE - tight-binding total energy
IVR - internal vibrational relaxation	TICT - twisted intramolecular charge transfer
kDa - kilo-Dalton	TOF - time of flight
kV - kilovolt	TOF-MS - time-of-flight mass spectrometry
L - liter	UIMS - User Interface Management Systems
LEED - low-energy electron diffraction	UV - ultraviolet
LEPD - low-energy positron diffraction	V - volt
LDEI - laser-driven electron impact	VLSI - very large scale integration
LIF - laser-induced fluorescence	VUV - vacuum ultraviolet
LIMS - laser ionization mass spectrometry	ZEKE - zero kinetic energy
LMMS - Large Molecule Mass Spectrometry	

DISTRIBUTION

No. of
Copies

No. of
Copies

OFFSITE

- 12 DOE/Office of Scientific and
Technical Information

G. Fisk
U.S. Department of Energy
Office of Basic Energy Sciences
ER-14, G-338/GTN
Germantown, MD 20545

C. Frank
U.S. Department of Energy
1000 Independence Ave SW
Washington, DC 20585

L. C. Ianniello
Deputy Associate Director
U.S. Department of Energy
Office of Basic Energy Sciences
ER-11, J-304/GTN
Washington, DC 20545

R. S. Marianelli
U.S. Department of Energy
Office of Basic Energy Sciences
ER-14, G-338/GTN
Germantown, MD 20545

ONSITE

- 2 DOE Richland Operations Office

L. Erickson, A5-10
D. E. Trader, A5-90

- 42 Pacific Northwest Laboratory

R. C. Adams, K6-52
W. J. Bair, K1-50
J. F. Bagley, K1-64
T. D. Chikalla, P7-75
G. H. Cunningham, K1-59
W. V. Discenza, K1-84
D. W. Dragnich, K1-46
S. K. Edler, K1-06 (5)
J. W. Falco, K6-78
R. M. Fleischman, K1-43
F. C. Hood, K1-60
A. F. Johnston, K1-44
M. L. Knotek, K1-48
W. W. Laity, K2-15
R. C. Liikala, K1-57
L. M. Martucci, P7-35
R. J. Mayer, K1-62
J. L. McElroy, P7-46
G. R. Petersen, K1-40
J.T.A. Roberts, K1-73
R. W. Root, B1-40
A. A. Shepherd, K1-55 (5)
B. D. Shipp, K1-73
G. M. Stokes, K1-74
J. L. Straalsund, K1-79
W. R. Wiley, A4-25
L. D. Williams, K1-41
G. L. Work, K2-51
Publishing Coordination
Technical Report Files (5)