EMSL 2001

Since its dedication at the beginning of fiscal year 1998, the Environmental Molecular Sciences Laboratory (EMSL) has demonstrated remarkable leadership in fundamental science at the Pacific Northwest National Laboratory (PNNL). Our scientists conduct intramural research at the highest level and serve as consultants, collaborators, mentors, and facilitators to extramural scientists. These important research partners make effective use of EMSL as a national user facility equipped with unique resources for addressing important scientific issues at the molecular level of enquiry. ***EMSL 2001*** is a snapshot of our capabilities and a sampling of our current activities.

Jean Futrell, Director, July 2001

Advanced Resources

EMSL provides advanced experimental and computational resources to scientists engaged in fundamental research on the physical, chemical, and biological processes that underpin environmental and other critical scientific issues. Resources available to users and resident staff include six research facilities:

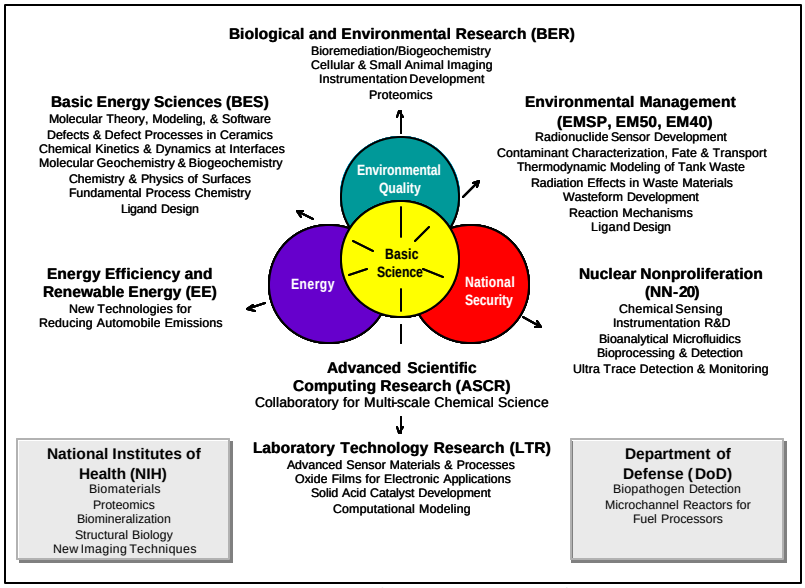
- **Molecular Science Computing Facility** for simulating complex molecular phenomena
- **High-Field Magnetic Resonance Facility** for structural biology and microimaging
- **High-Performance Mass Spectrometry Facility** for analyzing biomolecules
- **Interfacial & Nanoscale Science Facility** for characterizing interfaces, studying interfacial chemical reactions and processes, and synthesizing nanoscale materials and systems
- **Trace Detection Facility** for detecting and monitoring trace species
- **Optical Imaging & Spectroscopy Facility** for developing and using advanced optical techniques to characterize complex systems.

Intramural Research

EMSL research programs address complex problems relevant to DOE missions and support other government organizations. Additionally, EMSL staff plays a key role in major laboratory initiatives—Biological Sciences, Computational Sciences and Engineering, and Nanoscience and Nanotechnology.

Education

Educational internships provide graduate, undergraduate, and high school students; faculty; and postdoctoral fellows with challenging research opportunities with EMSL staff.

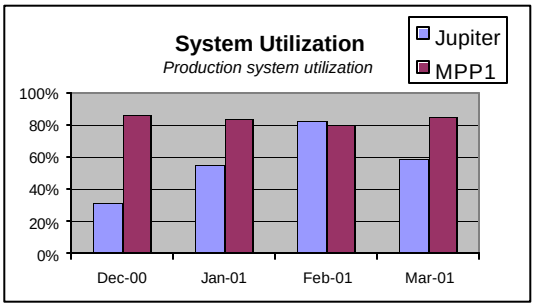


Research within the EMSL advances fundamental scientific knowledge on the physical, chemical, and biological processes that underlie the most critical issues facing the DOE.

User Facility Highlights

998 FY01 Users (cumulative through 3rd quarter)
47% onsite facility users
25 % remote facility users
28 % software users

MSCF enhancements. The Molecular Science Computing Facility (MSCF) provides one of the most highly valued resources to the EMSL user community. Year-to-date system availability of 99.3% is the highest availability rating ever achieved in MSCF and includes the major upgrade to NWmpp1 during February 2001. The high utilization rate achieved on NWmpp1 (FY01: 84%) continues the yearly increase trend since its install. The MSCF upgrade will enable EMSL to continue to address significant grand challenges while providing increased computational capacity for additional users.



EMSL user and collaborator points out the importance of user research facilities. In a special issue of *Chemical and Engineering News*, "Celebrating the ACS at 125" (March 26, 2001), Professor Mark Bussell (Western Washington University) writes about the importance of a significant research opportunity for undergraduate science majors. In his article, "Laying the Foundation", he points out that the importance of a significant research opportunity for undergraduate science majors is recognized across the spectrum of higher education. In fact, the American Chemical Society's Committee on Professional Training "strongly endorses undergraduate research as one of the potentially most rewarding aspects of the undergraduate experience." Professor Bussell put this belief into action and brought his undergraduate students to EMSL to work on catalyst characterization.

Helping solve materials science issues associated with the final optics assembly of the LLNL National Ignition Facility. Lawrence Livermore National Laboratory (LLNL) researchers (in collaboration with IC&E staff) are investigating materials science issues associated with the Final Optics Assembly of the LLNL National Ignition Facility (NIF). Optical materials, including fused silica and deuterated potassium hydrogen phosphate (DKDP), are being examined via x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (TOF-SIMS) to determine the source of surface and bulk laser damage sites. The damage sites, formed when the optics are irradiated by high power UV lasers during testing, render the optic unusable. Investigations to date have determined the identity of several impurities introduced during crystal growth and processing that may be responsible for some of the sites. Continuing work is directed toward developing a better understanding of the identity and local chemical environment of the impurities.

Comparing theory and experimental measurements of electronic structures of minerals. University of Washington Professors Fumio Ohuchi and Subrata Ghose (Department of Materials Science and Engineering and Department of Geological Sciences, respectively) are working with Don Baer and Mark Engelhard (IC&E) to examine the electronic structure of different but similar mineral phases. Although not widely examined, XPS valence band data provides complex but unique and useful information about electronic structure of materials that is best understood in the context of theoretical models.

MR imaging of colloid transport in Hanford sediment. Dr. Markus Flurry (Washington State University) is testing whether MR imaging can be used for visualizing the transport of colloids in Hanford sediment in order to determine whether colloid-facilitated transport might be a factor in the dispersal of radionuclides leaking from Hanford tanks. Working with Kevin Minard (MS&D), he has developed a magnetically labeled colloid whose presence enhances the NMR relaxation properties of surrounding water. Current efforts are underway to increase the degree of enhancement that is achievable in order to facilitate indirect colloid visualization with MR imaging.

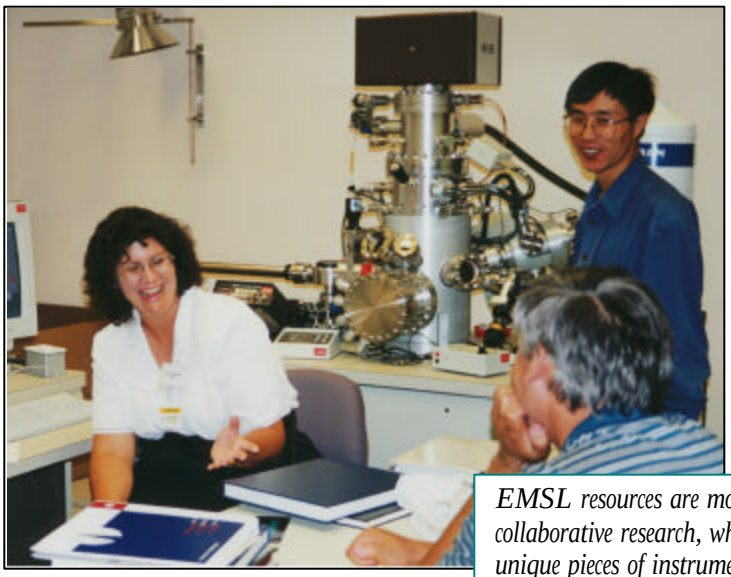
First characterization of boron chemical shift tensors. David Bryce, Myrlene Gee, and Roderick Wasylishen from the University of Alberta reported the first characterization of boron chemical shift (CS) tensors in the literature

[*J. Phys. Chem. A* **105**, 3633-3640 (2001)]. Boron, a half-integer quadrupolar nucleus, is a component of many glasses, including waste vitrification glasses, and has been studied extensively utilizing ^{11}B NRM. Despite a plethora of boron NMR studies and the very large known chemical shift range of boron, no boron CS tensors have previously been characterized. However, as commercially available magnet field strengths increase, the CS becomes increasingly important because it scales linearly with the field. Magnitude and relative orientation of the CS tensors may be important in such applications as obtaining quantitative results from rotational resonance experiments. The high field portions of the studies were carried out on the EMSL 750 MHz NMR spectrometer.

Characterizing sediment samples from an oil-contaminated aquifer. Todd Anderson and Derek Lovely from the University of Massachusetts and Ravi Kukkadapu (ED&S) have been studying the Fe valence speciation and mineralogy of sediment samples from an oil-contaminated aquifer in Minnesota. The samples originated from geochemical zones that are dominated by different terminal electron acceptors. Characterization of the structural environment of Fe(II/III) by Mössbauer spectroscopy indicates the biogeochemistry of Fe in the sediments is quite complex, and microorganisms in the aquifer are able to biodegrade hydrocarbons using Fe(III) in the sediments as an electron acceptor. A manuscript will soon be prepared from this work.

Examining NAPL dissolution behavior under dynamic conditions. Collaborative studies by the University of Arizona and PNNL examined non-aqueous-phase liquid (NAPL) dissolution behavior under dynamic conditions of flow and transport. NAPL dissolution behavior under conditions prevalent at the field scale is critical for conducting risk assessments and implementing appropriate remediation strategies for NAPL-contaminated sites. Experiments were performed in EMSL in an intermediate scale flow cell packed with sand and zones saturated with trichlorethene. Results indicate that non-uniform NAPL distribution, physical heterogeneity, and non-uniform flow significantly influenced the magnitude and location of NAPL dissolution. The results also stress that the presence of a NAPL phase cannot be dismissed if aqueous concentrations are only a fraction of expected equilibrium concentrations.

MR imaging of bacterial biofilms in porous media. Dr. Brian D. Wood (EMSL user from Biological Sciences, PNNL) is examining whether ^{1}H-NMR microscopy can be used to monitor the growth of bacterial biofilms in porous matrices in an effort to elucidate factors affecting bioremediation utility. Working with Kevin Minard (MS&D), he has been able to use MR microscopy to characterize the pore-scale architecture of model porous systems and measure the NMR relaxation properties for water inside live bacteria. The next steps in this project are determining whether the relaxation properties of intracellular water can be exploited for distinguishing the bacteria from their aqueous environment and visualizing their pore-scale distribution in a functioning bioreactor.

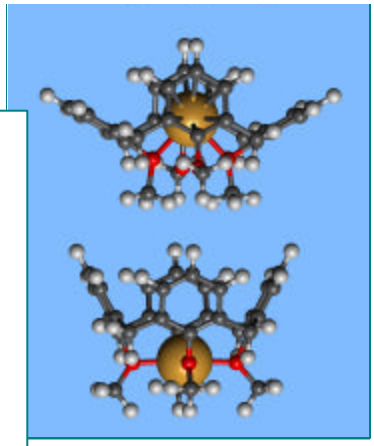


EMSL resources are most effectively used for collaborative research, where users gain access to unique pieces of instrumentation and interact with experienced staff members, who help them develop customized research strategies to take advantage of EMSL's extensive experimental and computational capabilities.

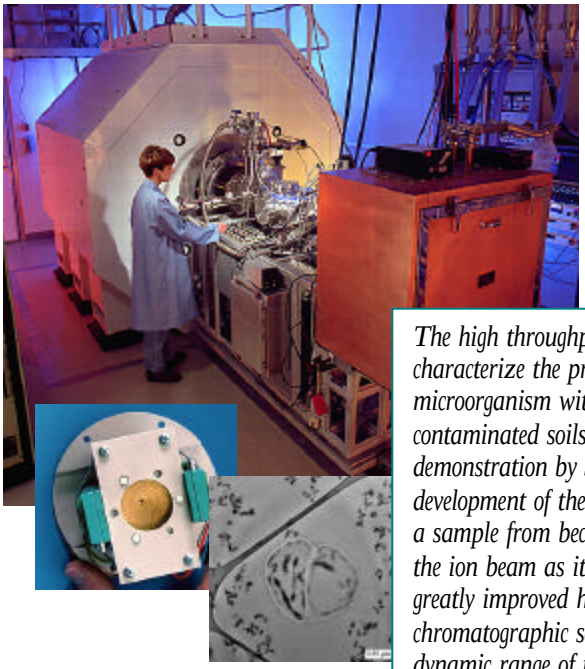
Intramural Research Highlights

Five scientific accomplishments by EMSL staff during the short years of our existence were among the 100 most important scientific discoveries supported by the Office of Science during the past 25 years http://www.sc.doe.gov/feature_articles_2001/June/Decades/:

Modeling and simulating environmental problems. Northwest Computational Chemistry Software *(NWChem)* is an advanced molecular modeling package featuring major design improvements over traditional codes, including new algorithms for computational chemistry and the high-level data and control structures needed to make parallel programs easier to write, maintain, extend, and use on a broad range of parallel computers. Developed in the mid-1990's by the Theory, Modeling, and Simulation group in EMSL, *NWChem* has been distributed to more than 300 sites worldwide, including most federal supercomputing centers and many universities. *NWChem* provides many methods for computing the properties of molecular systems by using quantum mechanics based on either molecular orbital theory or density functional theory. The software also can perform classical molecular dynamics and free-energy simulations of macromolecular and solution systems. For the first time, these approaches can be readily combined to perform mixed quantum mechanics and molecular dynamics simulations. Scientists are using it to run modeling and simulation studies of DOE's environmental problems and other subjects, from combustion to petrochemical zeolite catalysts. (BER)

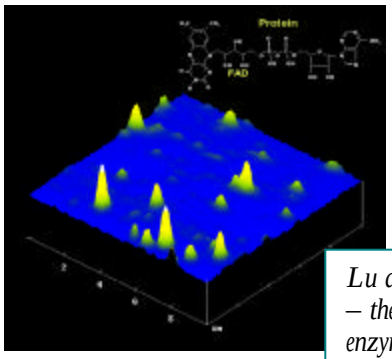


NWChem enabled a high level computational quantum chemical study of the complexation of the alkali cations Na^+ and Cs^+ with tetramethoxycalix[4]arene. Calixarenes provide an option for separating radioactive ions, such as Cs^+, from Hanford tank wastes. Although widely studied, the nature of the "host-guest" interactions, i.e., the interactions between the calixarene and the molecule or ion that is to be trapped, remains obscure. Results from the study showed that the host-guest interactions of this simple system are more complex that previously thought and provided new insight into the design of selective cation receptors.



Accelerating the study of proteins. New mass spectrometry techniques developed by Dick Smith and coworkers (MS& D) are the basis for measuring changes in the entire complement of proteins expressed in cells in a single experiment. This new approach can be used to monitor thousands to tens of thousands of proteins per day. The global perspective afforded by this new proteome measurement capability is diagnostic of changes within entire sets of cellular pathways and networks, thereby helping to identify those pathways key to a cell's state of development or response to a changing environment. (BER)

The high throughput approach has been used to characterize the proteome of Deinococcus radiodurans, a microorganism with potential for bioremediating contaminated soils and groundwater. Key to this successful demonstration by Smith and coworkers was the development of the ion funnel, a device that prevents ions in a sample from becoming lost by charge-charge repulsion of the ion beam as it is transferred into a mass spectrometer; greatly improved high pressure capillary liquid chromatographic separations; new methods for extending the dynamic range of measurements; and data processing methods that provide greater mass measurement accuracies for improved protein identification.



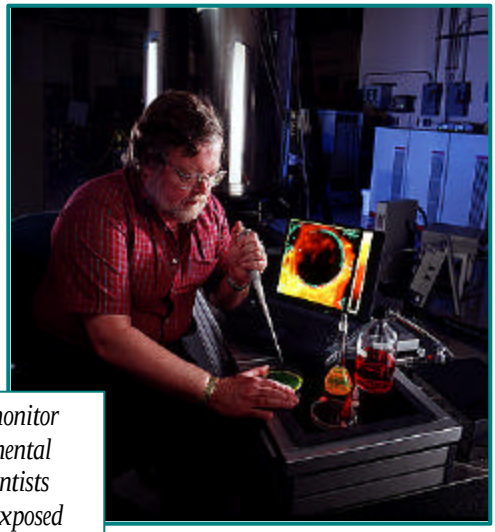
Optical probes for imaging single molecules. Real-time observation of individual enzyme molecules by Peter Lu (CS& D) and Sunney Xie (Harvard University) established single-molecule spectroscopy as one of the most important new methods for unraveling chemical dynamics in heterogeneous and complex chemical systems. In addition to their pioneering work on biological systems, Xie and Lu have developed and applied single-molecule spectroscopic methods for studying chemical dynamics in interfacial chemical systems, semiconductor nanoparticles, and nanostructures. (BER)

Lu and Xie observed – for the first time – the activity of nominally identical single enzymes in a sample to be widely variable and to change over time.

Preventing radioactive contamination. Collaborative research over the last 20 years between Rod Ewing of the University of Michigan and Bill Weber (IC&E) has established the conditions under which heavy-ion irradiation can be used to simulate radiation damage from alpha decay. Using heavy-ion irradiation and advanced characterization techniques, these researchers discovered that compositions in the gadolinium-zirconate system are extremely resistant to radiation damage by energetic particles, such as from the radioactive decay of plutonium. Plutonium is the key component in nuclear weapons and is radiotoxic with a half-life of 24,500 years. (BES)

The gadolinium-zirconate compounds absorb energy through the rearrangement of gadolinium, zirconium, and oxygen atoms within the crystal structure without becoming amorphous or otherwise structurally unstable. Computer simulation methods further confirmed the high mobility of disturbed atoms and ease of incorporating plutonium in the gadolinium zirconate structure. Thus, compositions in the highly durable gadolinium-zirconate system can lock plutonium into their structure while remaining extremely resistant to radiation damage. These gadolinium-zirconate systems are superior to the materials primarily being considered internationally for plutonium immobilization, such as gadolinium titanate, that readily undergo radiation-induced amorphization, a process that causes swelling, cracking and a 50-fold increase in the leach rate of plutonium. Gadolinium zirconate compositions, on the other hand, will remain unaffected for millions of years.

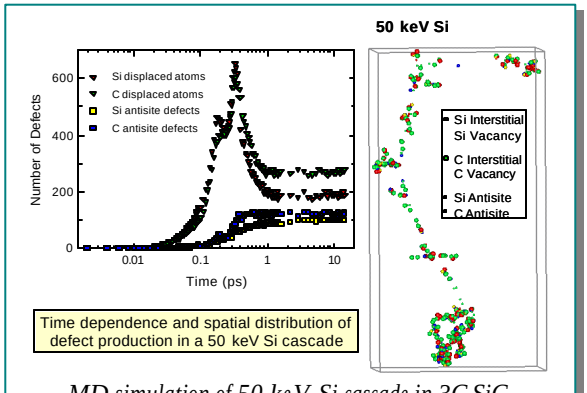
Observing chemical changes in living cells. Scientists from the MS&D group in EMSL and the Massachusetts Institute of Technology recently developed a system making it possible, for the first time, to simultaneously image "live" cellular systems using both optical microscopy and nuclear magnetic resonance (NMR) microscopy. The system combines new image contrast techniques, enhanced specificity to cellular events, and reduced NMR microscopy measurement times. The NMR imager works like a magnetic resonance imaging unit at a modern hospital, except that it examines much smaller collections of cells, down to a single cell and its nucleus. Furthermore, the new microscope reveals information about a cell's chemical composition and allows scientists to monitor changes in both the shape and chemical contents of the cells as they occur. (BER)



This noninvasive technique will enable scientists to monitor how live cells respond as they are exposed to environmental changes, such as heat, chemicals, and radiation. Scientists will also be able to see what happens when cells are exposed to multiple contaminants at the same time, and ultimately, to relate these responses to large-scale effects.

EMSL Research Highlights for 2001

First time atomic-scale simulation of energetic ion-solid interactions in silicon carbide. Bill Weber and Fei Gao (IC&E) used molecular dynamics methods to simulate the nature of high-energy ion-solid interactions and defect production processes in silicon carbide, a wide-bandgap semiconductor with great potential for high-temperature, high-power electronic devices and for nuclear power applications. These results [*Physical Review B* **63** (2001)] have provided new insights into the mechanisms of amorphization in silicon carbide and will provide the necessary atomic-level predictability for ion-implantation in nuclear environments. (BES, Materials Science and Engineering Division)



MD simulation of 50 keV Si cascade in 3C-SiC.

First observation of aromaticity in all-metal systems. Lai-Sheng Wang and his postdoctoral students Xi Li and Hai-Feng Wang (associated jointly with CS&D and Washington State University), and collaborators from Utah State University reported experimental and theoretical evidence of aromaticity in all-metal systems [X. Li, A.E. Kuznetsov, H.F. Zhang, A.I. Boldyrev, and L.S. Want, "Observation of All-Metal Aromatic Molecules," *Science* **291**, 859-861 (2000)]. This advance may lead to the development of totally new classes or aromatic inorganic and metal compounds. *Science* called attention to this work in a "Perspectives" article by D-K. Seo and J.D. Corbet, "Aromatic Metal Clusters," same issue (841-842), which comments that "Li *et al.*'s surprising aluminide clusters not only extend aromaticity into metallic elements but also bring to our attention other factors that govern structural patterns and the stability of solids." *Chemical and Engineering News* (February 5, p. 8) also covered this work in a "News of the Week" sidebar, "It's a Metallic Aromatic." (NSF and BER)

BES Chemical Sciences Research contributes to EM needs in the packaging of plutonium. The Fundamental Phase Partitioning in Supercritical Fluids Program (PI's: Clement R. Yonker and John L. Fulton) made an important contribution to the pressing need of EM in their moisture measurement of Pu and U oxides. In consultation with the local Richland Field Operations Office, guidance was given regarding the suitability of SFE (supercritical fluid extraction) for the development of a method to accurately measure residual water at levels near or below 0.5% wt in these complex oxide samples. In his letter of commendation to PNNL regarding this effort, Keith A. Klein, Manager, Richland Operations Office stated, "*Their expertise and advice are helping to resolve this issue. Their timely help will save DOE and its contractors thousands of man-hours and millions of dollars by avoiding flawed moisture measurement and packaging of plutonium*". (BES, Chemical Sciences Division)

Insight into dechlorination of carbon tetrachloride by Fe(II). Jim Amonette and Yuri Gorby (ED&S) published new insights into the mechanism by which carbon tetrachloride is degraded by Fe(II) adsorbed to mineral surfaces [Amonette, J. E., D. J. Workman, D. W. Kennedy, J. S. Fruchter, and Y. A. Gorby, *Environmental Science and Technology* **34**, 4606-4613 (2000)]. The key finding was that the rate-determining step of the dechlorination reaction is an unusual three-molecule (third-order) reaction, instead of the far more common two-molecule reactions that dictate most solution-phase reaction kinetics. As three-molecule reactions are extremely rare in solution, a mineral surface is needed to fix two of the reactants in a suitable geometry so that the third reactant can interact with both simultaneously. For the dechlorination of carbon tetrachloride by ferrous iron, electrons from two ferrous iron atoms are needed. When these iron atoms are adsorbed to the surface of goethite the reaction proceeds readily. No reaction occurs if goethite, or some other iron-sorbing surface, is absent. The role of the goethite surface is that of a catalyst. (EM/OST Subsurface Contamination Focus Area and LDRD)

Breakthrough in breaking chemical bonds. Jean Futrell, Julia Laskin, Anil Shukla and Eduard Denisov (MS&D) brought on-line a multi-sector tandem mass spectrometer with an ion cyclotron resonance (ICR) final stage which impacts ions on a self-assembled monolayer (SAM) surface and captures the products of surface-induced-dissociation (SID) reactions. The apparatus combines EMSL's patented ion funnel technology with radio-frequency ion optics and a novel ICR cell designed by Steve Barlow (MS&D). First performance tests of this research instrument demonstrated unprecedented sensitivity and accuracy and suggested potential applications to analytical problems.

Preliminary data demonstrating a hundredfold improvement in sensitivity in peptide sequencing—an essential step in proteomics mass spectrometry—was presented at the annual conference of the American Society for Mass Spectrometry in May 2001. (BES, Chemical Science Division)

Ion trapping at molecularly sculpted oil–water interfaces elucidates solvation forces near membranes. An invited feature article by K. Wu, M. Iedema, G. Schenter, and J. Cowin, "Sculpting the Oil–Water Interface to Probe Ion Solvation," provided the cover illustration for the April 5 issue of *The Journal of Physical Chemistry* [*J. Phys. Chem. B* **105**, 2483–2498 (2001)]. Transport across oil–water interfaces determines the ability of biological cells to control the movement of ions ands molecules across cell membranes; in addition, many industrial processes involve transport across, or reactions at, the interfaces of emulsions of organic species and aqueous solutions. Many aspects of these important processes are poorly understood. The paper reviews recent CS&D research, with theoretical contributions from TM&S, probing ion transport and solvation in composite films whose geometry is precisely controlled using a "soft-landed" deposition technique developed in EMSL. This allows the fabrication of structured interfaces that mimic membranes or interfaces in biology and electrochemistry. The ion motion can be followed with high sensitivity by monitoring the electric potential generated by the process. Such experiments have yielded unique information on details of the solvation process, and on the nature of ion transport in organic glasses. (BES, Chemical Sciences Division)

Low temperature NMR spectroscopy of metalloproteins and model compounds. Andrew Lipton, Robert Heck, Jennifer Ackerman, and Paul Ellis (MS&D) have been advancing low temperature NMR metalloproteins experiments on several fronts. Current experiments focus on how water bound to a metal (Mg^{2+}, Ca^{2+}, and Zn^{2+}) in a biological system is reflected in the magnetic resonance parameters of the reporting metal center. To this end they have been baselining their investigation by examining the inhibited form of two proteins carboxypeptidase and carbonic anhydrase, and initiating work on Ape1 (^{25}Mg and ^{43}Ca experiments in collaboration with LLNL). The first result has been published as a communication in the *J. Am. Chem. Soc.* (JACS). The editors of JACS found the paper to be of sufficient interest that it was also highlighted in *Chemistry & Engineering News* [C&E News **79**, 6, 9 (2001)]. (NIH and BER)

90% NOx emissions reduction milestone achieved. Researchers from the IC&E group demonstrated greater than 90% NOx reduction in thermal catalyzed reactions over zeolite-based catalysts. A key piece of their work was identifying the important organic reductant molecule that is formed in the plasma. Concurrent with these results, more recent experimental tests by researchers in CS&D on PNNL-designed reactors have likewise demonstrated greater than 90% NOx conversion. (EE)

Exciting new epitaxially grown material. Scott Chambers (IC&E) has preliminary evidence that molecular beam epitaxial grown Co-doped TiO_2 anatase on $SrTiO_3$(001) is a ferromagnetic semiconductor at room temperature. This result is significant in the field of spintronics because such materials are needed to achieve spin-polarized carrier transport in semiconducting structures without cryogenic cooling. Films grown at PNNL were subsequently tested for magnetic properties at IBM Almaden Research Center and shown to be ferromagnetic with magnetization loops that exhibit superior hysterisis compared to those published in *Science* **291**, 854-856 (2001). Ongoing work focuses on determining the mechanism for ferromagnetic behavior in this material. (PNNL Nanoscience and Nanotechnology Initiative)

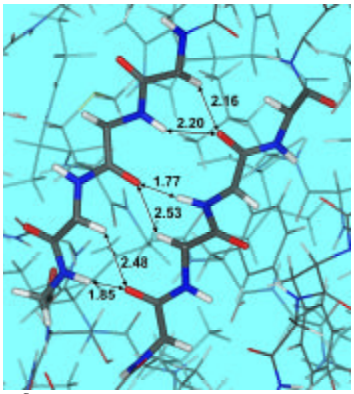
Sub-watt power using an integrated fuel processor and fuel cell generates an equivalent power of 10 mW to 500 mW_e. Evan Jones, Jamie Holladay, Steve Perry, Rick Orth, Bob Rozmiarek, John Hu, Max Phelps, and Consuelo Guzman have been working with Case Western Reserve University to develop and demonstrate this technology for the Defense Advanced Research Projects Agency. A sub-watt power system is being developed as an alternative to conventional battery technology to better meet energy and power densities needed for operating wireless electronic devices, such as microsensors and microelectromechanical systems. This system integrates a microscale fuel processor, which produces a hydrogen-rich stream from liquid fuels, such as methanol and butane, and a microscale fuel cell, which uses the hydrogen as fuel to produce electric power. (DARPA)

Insight into DNA repair using the 900 MHz narrow-bore NMR. Using the newest in NMR technology—a narrow-bore 900 MHz nuclear magnetic resonance (NMR) spectrometer (precursor to the 900 MHz wide-bore NMR under development for PNNL)— David Lowry, Joe Ford, and David Hoyt (MS&D) and David Wilson (LANL)

have for the first time been able to study DNA repair enzymes under normal biological conditions. Many enzymes that repair damaged DNA must do so by first simultaneously binding and stretching the DNA, and breaking a water molecule in two. The studies focused on one of a class of DNA repair enzymes called human Ape1. This class is distinguished by a histidine, common amino acid at the site where the DNA is repaired; however, its role in DNA repair, *i.e.*, whether it is used to bind the DNA, stretch the DNA, or break the water molecule in two, was previously unknown. The researchers showed that in the case of Ape1, the role of histidine is primarily to stretch the DNA. (BER)

Molecular dynamics simulations of the RasGAP protein complex illuminate a potential mechanism. Haluk Resat, T. P. Straatsma, David A. Dixon, and John H. Miller (TM&S) have been studying the Ras family of GTPases. Mutants of Ras are found in 25 to 30% of all human tumors and are insensitive to the negative regulatory action of GAPs. All known oncogenic mutants of Ras map to a small subset of amino acids and one of these, Glutamine (Gln) 61, is particularly important because virtually all mutations of this residue eliminate sensitivity to GAPs. Despite its obvious importance for carcinogenesis, the role of Gln 61 in the GAP stimulated GTPase activity of Ras has remained a mystery. Our long time molecular dynamics simulations of the p21ras-p120GAP-GTP complex suggest that the local structure around the catalytic region can be different from that revealed by the x-ray crystal structure. It was determined that Arg789 may play a dual role in generating the nucleophile as well as stabilizing the transition state for P-O bond cleavage. The work coupled with quantum chemical simulations clearly shows that charge balance in the active site is key to cleavage of the GTP [H. Resat, T. P. Straatsma, D. A. Dixon, and J. H. Miller, *Proc. Nat'l. Acad. Sci., USA*, **98**, 6033 (2001)]. (BER and LDRD)

Weak hydrogen bond may be key to protein folding. David A. Dixon and Benjamin P. Hay (TM&S) along with collaborators Rubicelia Vargas and Jorge Garza from the Universidad Autonóma Metropolitana-Iztapalapa have been studying the C^{α}-H•••O=C hydrogen bond interactions in N,N-dimethylformamide dimers. High level *ab initio* calculations have been used to compute electronic association energies and association enthalpies for three dimer geometries and provide a lower limit of –2.1 kcal/mol for the C^{α}-H•••O=C hydrogen bond. A linear correlation between C-H•••O bond energies and gas phase proton acidity was then established and used to estimate values for the dissociation energy of the C^{α}-H•••O=C hydrogen bond in a protein. The magnitude of this interaction, roughly half the strength of the N-H•••O=C hydrogen bond, suggests that C^{α}-H•••O=C hydrogen bonding interactions represent a hitherto unrecognized, significant contribution in the determination of protein conformation. This work was published in the *Journal of the American Chemical Society* **122**, 4750 (2000) and highlighted in *Chemical and Engineering News*, May 8, 2000, p. 15. (EMSP and BER, CONACYT Fellowship)



C^{a}-H•••O=C hydrogen bonds in the b-sheet formed by the protein called Achrobacter protease I. Numbers indicate estimated distances (in angstroms) between the hydrogen atoms (white) and oxygen atoms (red). Carbon atoms are shown in gray and nitrogen atoms in blue.

Accurate energetics of the first few water clusters from first principles. Accurate determination and analysis of interaction energies in water clusters provides indispensable information needed for the development of models that are transferable across different environments (solid, liquid, and clusters) and length scales. Currently, in the absence of any experimental information, the only reliable information about the energetics of water clusters is provided by theoretical calculations. EMSL researchers Sotiris Xantheas and Robert Harrison have used the *NWChem* suite of codes on the 512-node IBM SP in the Molecular Science Computing Facility to performed large, computationally demanding, *ab initio* electronic structure calculations to obtain accurate energetics for the water trimer through pentamer global ring minima and four low-lying hexamer isomers (cage, prism, book, cyclic S_6). Additional calculations, accomplished at the very highest levels of theory, indicate that the determined energetics are accurate to within 0.2 kcal/mol. Non-additive contributions have been shown to contribute significantly to the total cluster energies for configurations representative of clusters, liquid water and ice. Estimates of the percentage contributions to the total energies from non-additive (three-body and higher) terms range from 39% for liquid water to 31-34% for clusters (n=2-21) and 32% for ice Ih. This work has been submitted for publication in the *Journal of Chemical Physics*. (BES, Chemical Sciences Division and BER)

Education Highlights

Nancy Ruzycki, a graduate student (Tulane University), who has been collaborating with IC&E staff for several years, was selected by DOE to attend the **Nobel Laureate convention** in Lindau, Germany on June 25-29. Nancy reports:

> *As a participant, I found the week to be an invaluable experience, not only for the chance to discuss and gain knowledge from the laureates, but also to meet and interact with other young American researchers from around the country about their graduate school and research experiences. I found that the research done here at PNNL, along with my thesis research to be of the highest caliber, and it made me more committed to becoming a research scientist and continuing my investigations.*

Zdenek Dohnálek received the **2000 M.T. Thomas Award for Outstanding Postdoctoral Achievement** *for his experimental and theoretical contributions to understanding the crystallization, morphology, and properties of amorphous solid water, and to the molecular beam synthesis of chemically tailored nanoporous films."* Zdenek was a Postdoctoral Fellow with Bruce Kay (CS&D) and joined EMSL staff last August.

Dr. Norman Chonacky, Jeffrey Holmes, and James Thomas are working with the EMSL to develop a new junior-senior undergraduate laboratory course sequence in **Bio-Medical Engineering (BME) at Columbia University**. Students will use radio linkages to the Internet to connect to EMSL's electronic laboratory notebook and remote instrument control capabilities. These combined capabilities will, for the first time, integrate phenomena, data, theory, and students' work in and across the several disciplines, courses, faculty, and physical locations.

Dr. Timothy Veenstra hosted a **scientist student teacher (SST) team from Prosser High School** that was charged with extracting phosphorylated peptides from the **proteome of *Deinococcus radiodurans***. Their work resulted in the submission of an abstract to a regional ACS meeting and was also included within a presentation to the Department of Energy.

Hanford High School science teacher Brian Palmer worked with researchers in the IC&E group to set up **a remote classroom** that allows his students to analyze samples using an EMSL multi-probe system that includes x-ray photoelectron spectroscopy. Over the school year, the students visited EMSL weekly to load samples and conducted research from their classroom.

Sabbatical Leaves at EMSL

Professor Paul G. Tratnyek from the Department of Environmental Science and Engineering at **Oregon Graduate Institute** spent a sabbatical working with Jim Amonette, Zheming Wang, Ravi Kukkadapu (ED&S), and Don Baer (IC&E) on a variety of issues related to the redox chemistry of metallic iron and humic substances. He also was a co-principal investigator on a successful proposal to DOE's Basic Energy Sciences Program.

Professor Barbara Balko from the Department of Chemistry at **Lewis and Clark College** spent a sabbatical working with Jim Amonette (ED&S) on the electrochemistry of structural and sorbed Fe associated with smectite clay minerals.

Professor Eric Altman from the department of Chemical Engineering at **Yale University** spent a sabbatical working with Scott Chambers and Yong Liang (IC&E) to synthesize and characterize single-crystal films.

Professor Paul B. Shepson from **Purdue University** spent a sabbatical working with Jim Cowin (CS&D) and Len Barrie and others in the Atmospheric Chemistry Group. Professor Shepson is a specialist in atmospheric ozone chemistry, photochemistry and chemical kinetics in the atmosphere, and the development of analytical methods for trace-level atmospheric measurements.

Significant Awards and Events

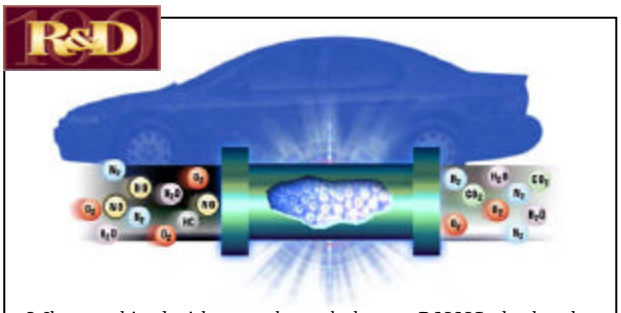
Robert Wind (MS&D) received the **2001 Discover Magazine Technology Award** in the Health Category for his contributions to the development of the Combined Optical and Magnetic Resonance Microscope. Robert received his award at a ceremony June 11 in New York.

Dear Dr. Wind:

I want to extend my personal congratulations to you for winning this year's Discover Magazine Innovation Award. Your invention of the combined optical and magnetic resonance microscope promises to improve our understanding of the living human cell. It is exciting that your novel instrumentation has the potential to measure the effectiveness of chemotherapy. I am proud to know that researchers like yourself are members of the Department of Energy laboratory family.

Please convey my congratulations to your team.
Signed: Spencer Abraham, Secretary of Energy

2001 R&D 100 Award: Catalyst Materials for Plasma-Catalysis Engine Exhaust Treatment
Lou Balmer-Miller*, Stephan E. Barlow*, Suresh Baskaran, Darrell R. Herling, Russell G. Tonkyn*, Alexander Panov* (*EMSL), John Hoard (Ford Research Laboratory), Galen Fisher (Delphi Research Labs)



When combined with a nonthermal plasma, PNNL-developed catalyst materials enable the plasma-catalysis technology that is perhaps the most promising option for removing NOx in exhaust from next-generation energy-efficient vehicles.

The nation's three major automobile manufacturers have participated in an R&D program with PNNL to develop this technology and explore its use in actual vehicles. Delphi Automotive, previously part of General Motors, now is working separately with PNNL to develop optimal system designs for a commercial plasma-catalysis engine exhaust system that uses these materials together with a non-thermal plasma. This work was also awarded the Department of Energy's **2001 CIDI Combustion and Emission Control Program Special Recognition** for outstanding achievement in research for the Non-Thermal Plasma CRADA.

Chris Parkinson (Instrument Development Group) received a **Federal Laboratory Consortium Technology Transfer Award** in May 2001 for his efforts in commercializing the EMSL Publisher software. EMSL Publisher is a powerful word processing and presentation tool that offers the unique ability to run the same software on any computer platform.

Bruce Kay (CS&D) was elected a **Fellow of the American Physical Society**, November 2000 *"for his innovative use of molecular beams and laser spectroscopy to elucidate chemical kinetics and dynamics of sorption, diffusion, phase transformation, and solvation at environmentally-relevant aqueous and oxide interfaces."*

Don Baer (IC&E) was elected a **Fellow of the AVS** (formerly the American Vacuum Society), May 2001 *"for creative research and for professional efforts that have led to more accurate applications of surface analysis methods to complex problems, including an understanding of how impurities and defects influence the stability and interfacial properties of metals, oxides, and minerals."*

Nancy Foster-Mills (ED&S) received the **2001 Chet Cooper Mentor-of-the-Year** award in December 2000 and the **Fitzner-Eberhardt Award** in June 2001, in recognition of her contributions in mentoring students and in advancing science education.

Mary Lipton (MS&D) was honored as **PNNL's 2001 Woman of Achievement** at a March 2001 award ceremony. She was recognized for her outstanding professional endeavors, personal development, and efforts to improve our community.

Yali Su (IC&E) received the **Best Presentation Award** (Salt Processing Project TFA FY-2000 Annual Program Review, November 2000, Atlanta, Georgia) for her summary of results achieved from recently conducted Cs adsorption/desorption experiments. The results from these experiments will aid DOE in selecting the best process for Cs separation at Savannah River sites, and will be used to develop engineering solutions to process upsets that result in minor temperature excursions.

EMSL's Theory, Modeling and Simulation Directorate hosted a special two-day **Computational Chemistry Users Meeting** June 18-19. Close to 70 researchers from the US and abroad attended. The meeting focused on users of the Molecular Science Software Suite (MS^3)—the high performance computational chemistry software *NWChem*, its associated user interface *Ecce*, and the underpinning set of high performance tools *ParSoft*—as well as chemistry users of the Molecular Science Computing Facility. The two-day meeting featured:

- A half-day session of presentations by MS^3 developers highlighting the current functionality and capabilities of the software as well as potential new capabilities
- Two half-day sessions comprised of 16 invited talks by users of the MS^3 and the MSCF describing their research and needs for new capabilities
- A half-day tutorial for people who wish to develop computational chemistry software within *NWChem*
- An *Ecce* installation tutorial, and
- A poster session.

Highlights of this event, including speaker presentations and a gallery of pictures, can be viewed at: http://www.emsl.pnl.gov:2080/mscf/usersmeeting

A **Joint Institute for Nanoscience and Nanotechnology** between the University of Washington and PNNL that facilitates collaborative research among professor, students, and scientists was formalized in April. Under this institute, exchange of students, faculty, and EMSL staff will be fostered in order to bring the capabilities of both institutions to bear on Nanoscience and Nanotechnology scientific challenges.

Six staff members from MS&D attended the **42nd Experimental Nuclear Magnetic Resonance Conference** (ENC) held in Orlando, Florida, March 2001 where they demonstrated simultaneous NMR experiments with the EMSL 600 MHz instrument located in Richland, Washington and Varian NMR Systems/Oxford Instruments new 900 MHz narrow-bore NMR system located in Oxford, England. Audio communication and live camera feeds from each location allowed ENC participants to view work around the 900 MHz and 600 MHz NMRs. Real time results allowed the experimental data collected from both spectrometers to be contrasted.

John Zachara (Associate Director, Environmental Dynamics & Simulation) organized and chaired the **Second EMSP Vadose Zone Workshop** (November, 2000) that included over 100 participants from DOE, universities, national laboratories, and the Hanford Site (regulators and contractors). New scientific findings from EMSP investigators were identified that may now be applied to resolve key scientific issues at Hanford and to direct future EMSP research that is needed to devise credible long term closure and remediation strategies for the Hanford tank farms and defense non-aqueous-phase liquid contaminated groundwater.

The Pacific Northwest National Laboratory participated in the **Supercomputing 2000** Trade Show held November 2000 in Dallas, Texas. Research in the areas of Atmospheric Science, Computational Biology, Computer Science, Computational Chemistry, Engineering, Reactive Transport, and Applied Mathematics was highlighted.

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