

EMSL Monthly Report
February 2003

The W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL) is a U.S. Department of Energy (DOE) national scientific user facility located at Pacific Northwest National Laboratory (PNNL) in Richland, Washington. EMSL is operated by PNNL for the DOE Office of Biological and Environmental Research. At one location, EMSL offers a comprehensive array of leading-edge resources in six research facilities.

Access to the capabilities and instrumentation in EMSL facilities is obtained on a peer-reviewed proposal basis. Users are participants on accepted proposals. Staff members work with users to expedite access to the facilities and scientific expertise. The Monthly Report documents research and activities of EMSL staff and users.

Research Highlights

Solid-State NMR Spectroscopy of Quadrupolar Nuclei at High Magnetic Field Strengths

DL Bryce,^(a) KW Feindel,^(a) MA Forgeron,^(a) M Gee,^(a) KJ Ooms,^(a) and RE Wasylshen^(a)

(a) University of Alberta, Edmonton, Alberta, Canada

High-field nuclear magnetic resonance (NMR) spectroscopy has been used to characterize "traditionally difficult" quadrupolar nuclei that are important in materials science and structural biology. The use of high applied magnetic field, B_0 , strengths is critical because it facilitates measurement of the chemical shift (CS) tensor and reduces the line width of the central transition arising from the second-order quadrupolar interaction. NMR investigations of quadrupolar nuclei are capable of providing subtle information about the orientation dependence of the CS and electric field gradient at a particular nuclear site. During the last three visits at EMSL, high-field ^{95}Mo NMR spectra of several molybdate salts and mesitylenetricarbonylmolybdenum(0) were successfully obtained, as well as ^{53}Cr NMR spectra of a series of solid chromate salts and one dichromate salt (Figure 1). The ^{95}Mo NMR work on mesitylenetricarbonylmolybdenum(0) is summarized in a full manuscript, published in *Physical Chemistry Chemical Physics*. The ^{53}Cr QCPMG NMR spectra of the chromates—the first reported chromium NMR studies of diamagnetic solids—were presented at The Canadian Society for Chemistry conference held in Vancouver, British Columbia, in June 2002.

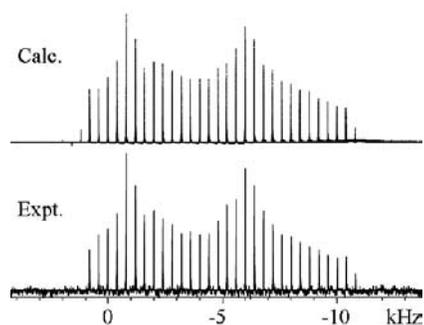


Figure 1. Calculated and experimental ^{53}Cr Quadrupole Carr-Purcell Meiboom Gill (QCPMG) NMR spectra of solid K_2CrO_4 .

Au₂₀: A Tetrahedral Cluster

J Li,^(a) X Li,^{(a)(b)} HJ Zhai,^{(a)(b)} and LS Wang^{(a)(b)}

(a) W.R. Wiley Environmental Molecular Sciences Laboratory

(b) Washington State University, Richland

It is well known that the properties of small groups of atoms or molecules—clusters—depend on their size. For many years, research has focused on determining at what size the properties of the cluster approach the bulk properties. Recent experiments conducted in Professor Wang's laboratory at Washington State University have shown that small clusters of gold atoms are extremely stable and have an extremely large band-gap energy and high electron affinity. The band-gap energy is greater than, and the electron affinity is comparable to, those of C₆₀ (known to be very stable). This very stable gold cluster molecule has a structure similar to a fragment of bulk gold but with very different physical properties. These observations suggest that Au₂₀ may be a building block unit for the creation of new materials with unique physical and catalytic properties. Figure 2 shows one optimized structure of Au₂₀.

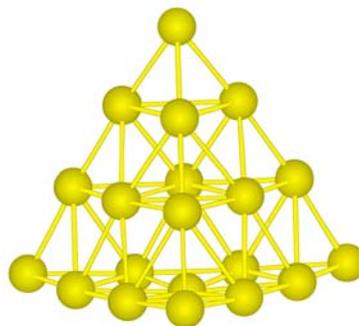


Figure 2. Optimized Au₂₀ structure (*T_d*).

This research was published in *Science* 299(7), 864-867 (2003), and accounts of the work appeared in *Chemical & Engineering News* (February 10, 2003), *The Hanford Reach* (February 24, 2003) and the Tri-City Herald.

Performance of Coupled Cluster Theory in Thermochemical Calculations of Small Halogenated Compounds

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(a) Pacific Northwest National Laboratory

(b) Washington State University, Pullman

(c) W.R. Wiley Environmental Molecular Sciences Laboratory

Atomization energies at 0 K and heats of formation at 298 K were obtained for small, halogenated molecules using coupled cluster theory. The study included noniterative, quasiperturbative triple excitations and calculations with large basis sets (up through augmented septuple zeta quality in some cases). A composite theoretical approach was adopted to achieve near chemical accuracy (± 1 kcal/mol) in the thermodynamic properties, and incorporated estimated complete basis set binding energies based on frozen-core coupled cluster theory energies and (up to) five corrections: (1) a core/valence correction; (2) a Douglas-Kroll-Hess scalar relativistic correction; (3) a first-order atomic spin-orbit correction; (4) a second-order spin-orbit correction for heavy elements; and (5) an approximate correction to account for the remaining correlation energy. The last of these corrections is based on a recently proposed approximation to full configuration interaction

via a continued fraction approximant for coupled cluster theory. Failure to consider corrections (1) to (4) can introduce errors significantly in excess of the target accuracy of ± 1 kcal/mol. Although some cancellation of error may occur if one or more of these corrections are omitted, such an occurrence is by no means universal and cannot be relied upon for high accuracy. The accuracy of the Douglas-Kroll-Hess approach was calibrated against both new and previously published four-component Dirac Coulomb results at the coupled cluster level of theory. In addition, vibrational zero-point energies were computed at the coupled cluster level of theory for those polyatomic systems lacking an experimental anharmonic value.

Mössbauer and Optical Spectroscopic Study of Temperature and Redox Effects on Iron Local Environments in an Fe-Doped (0.5 mol% Fe₂O₃) 18Na₂O-72SiO₂ Glass

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(c) University of Arizona, Tucson

Local environments of ferric and ferrous irons were systematically studied with Mössbauer (at liquid helium temperature, 42 K) and ultraviolet-visible near-infrared spectroscopic methods for various 18Na₂O-72SiO₂ glasses doped with 0.5 mol% Fe₂O₃. These were prepared at temperatures of 1300-1600°C in ambient air or at 1500°C under reducing conditions with oxygen partial pressures from 12.3 to 0.27x10⁻⁷ atmospheres. The Mössbauer spectroscopic method identified three types of local environments, which were represented by the Fe³⁺ sextet, the Fe³⁺ doublet, and the Fe²⁺ doublet. The Fe³⁺ sextet ions were assigned to "isolated" octahedral ions. Under reducing conditions, the octahedral Fe³⁺ ions were readily converted into octahedral ferrous ions (Figure 3). The Fe³⁺ doublet exists both in octahedral and tetrahedral environments, mainly as tetrahedral sites in the reduced samples. The tetrahedral ions were found to be stable against reduction to ferrous ions. The Fe²⁺ doublet sites existed in octahedral coordination. Combining results from both spectroscopic studies, the 1120- and 2020-nm optical bands were assigned to

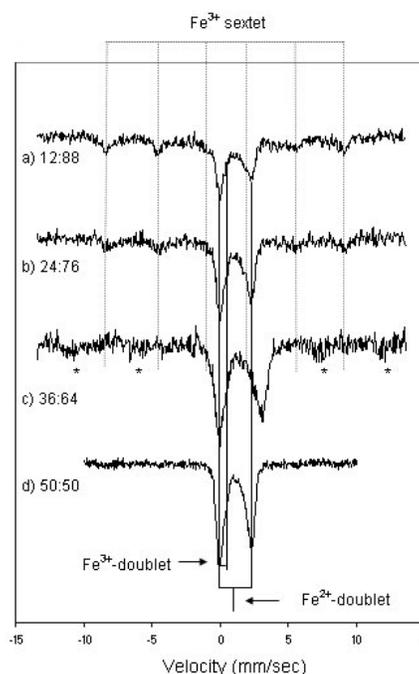


Figure 3. ⁵⁷Fe Mössbauer spectra of glasses melted at 1500°C in air under reducing atmospheres (a) 12CO/88CO₂, (b) 24CO/76CO₂, (c) 36CO/CO₂, and (d) 50CO/50CO₂.

octahedral ferrous ions with a different degree of distortion rather than different coordinations. Further, the 375-nm band was assigned to the transition of octahedral ferric ions that are sensitive to the change of oxygen partial pressure in glass melting, and 415-, 435-, and 485-nm bands were assigned to the transitions of the tetrahedral ferric ions that are insensitive to oxidation states of the melt. The effect on glass immiscibility of ferric and ferrous ions with different coordination environments was elucidated.

Analysis of Helium Retention in SiC as a Function of Irradiation and Annealing Using Ion Beams

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(c) Brigham Young University, Provo, Utah

(d) Pacific Northwest National Laboratory

Silicon carbide (SiC) has been proposed for coating applications in advanced reactor designs, so studies of its behavior in the presence of ion irradiation and fission products are of interest. Retention of helium in single-crystal 6H-SiC was studied as a function of irradiation dose and annealing temperature using both Nuclear Reaction Analysis (NRA) and Time-Of-Flight Elastic Recoil Detection Analysis (TOF ERDA). Ions of $^3\text{He}^+$ were implanted at 40 keV in SiC to a depth of ~ 360 nm at room temperature. NRA was performed using 1.0 MeV D^+ and the $^3\text{He}(\text{D},\alpha)^1\text{H}$ reaction (Figure 4).

No change in the He profile was seen for the irradiation dose up to $4 \times 10^{18} \text{ D}^+/\text{cm}^2$ at room temperature. Isochronal annealing of the SiC between 300 and 1400 K also showed no significant helium loss. Subsequently, a sample was irradiated with D^+ at 900 K and again at 1100 K. No loss of helium associated with irradiation was seen for the dose up to $1.4 \times 10^{18} \text{ D}^+/\text{cm}^2$. Annealing the sample above 1400 K resulted in thermally activated loss of He. TOF ERDA measurements were performed using 44 MeV $^{129}\text{I}^{10+}$ for both irradiation and analysis. Depth profiles of the He distribution showed no significant change under I bombardment with an ion fluence up to $\sim 10^{14} \text{ cm}^{-2}$ at room temperature. NRA was performed on the implanted sample subjected to ERDA analysis. The helium profiles for regions subjected to I irradiation were similar in shape to those with no I irradiation.

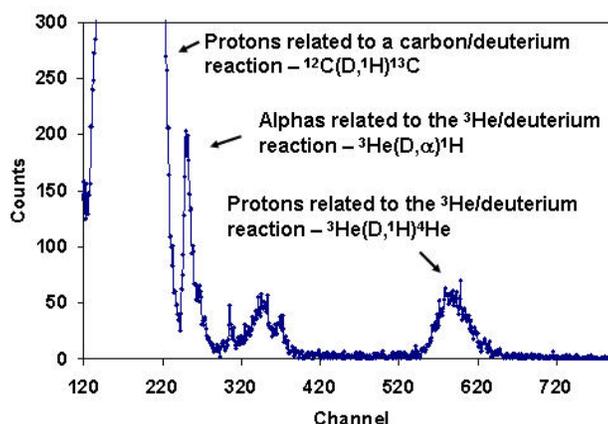


Figure 4. Nuclear reaction products from the ^3He -implanted region of the SiC sample.

Redox Properties of Water on the Oxidized and Reduced Surfaces of CeO₂(111)

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This summary describes the X-Ray Photoelectron Spectroscopy (XPS) and Temperature-Programmed Desorption (TPD) results from probing the surface chemistry of water on the oxidized and reduced surfaces of a 500-Å epitaxial CeO₂(111) film grown on yttria-stabilized ZrO₂(111) (Figure 5). Results show that epitaxial films of CeO₂(111) on YSZ(111) are readily reduced by annealing in an Ultra-High Vacuum (UHV) at temperatures

between 773 and 973 K. XPS analysis indicates that the majority of reduction is located in the outer layer of the CeO₂(111) film, with levels of surface reduction reflective of a suboxide of ceria achieved by annealing above 840 K. TPD and XPS studies indicate that water does not oxidize Ce³⁺ sites on the reduced CeO₂(111) surface under UHV conditions below 650 K. In fact, XPS results suggest that water exposure at 650 K increases the level of CeO₂(111) surface reduction, presumably by stabilizing Ce³⁺ sites at the surface that result from bulk-to-surface diffusion of oxygen vacancies. The reactivity of Ce³⁺ surface sites toward water likely depends on the surface termination and morphology. In particular, while water was unable to oxidize Ce³⁺ sites on atomically flat CeO_{2-x}(111) surfaces, water has been observed to oxidize Ce³⁺ sites on reduced CeO₂ powders and lattice mismatched films of CeO_{2-x}(111) on Ru(0001). In general, this implies that the diverse surfaces of crystalline nanoparticles of ceria may simultaneously support oxidation and reduction reactions of the same molecule on different parts of the particle, with the flow of electronic defects between different surfaces on the same particle potentially promoting resurfacing of the particle.

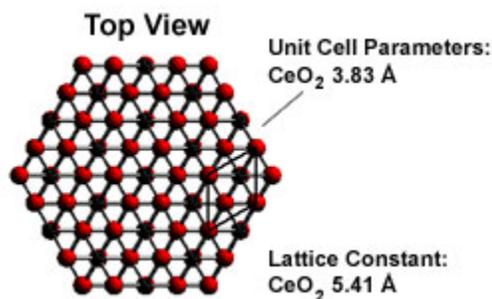


Figure 5. Surface structure of CeO₂(111).

Proteome Analysis of a Breast Carcinoma Cell Line Overexpressing the HER2/neu Oncogene

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(a) University of California, San Francisco

Significant progress has been made in analyzing the proteome of small numbers of cells, an essential requirement if mass spectrometry is to be used to identify and characterize breast carcinoma cells. Lysate from 5,000 cells of a human breast cell line, MCF7, were used for light and heavy solid-phase isotope labeling. For this small-scale sample processing, immobilized trypsin was used for protein digestion. Cys-containing peptides were then labeled and simultaneously captured onto the solid phase by adding 5 mg of beads (light or

heavy isotope coded) to each sample and incubating at room temperature for 2 hours with constant shaking. The recovered Cys-containing peptide sample was analyzed by the liquid chromatography-Fourier transform ion cyclotron resonance (LC-FTICR) system using the 15- μm i.d. separation capillary. Of the 400 nanograms of peptide mixture recovered, approximately 20 were used for DREAMS (Dynamic Range Enhancement Applied to Mass Spectrometry) LC-FTICR mass spectrometry analysis to extend the dynamic range of measurements. The analysis of the normal spectra resulted in the observation of a total of 1,207 solid-phase isotope-coded affinity tags (ICAT)-labeled peptide pairs from MCF7 cells. The set of DREAMS mass spectra revealed 1,497 solid-phase ICAT-labeled peptide pairs, of which 1,177 were "new" peptide pairs not detected in the normal spectra. Thus, a combined total (excluding overlap) of 2,384 unique peptide pairs from the MCF7 cells were observed in this analysis, starting from only 5,000 cells for each preparation.

Characterization of Single-Crystal Oxide Interfaces

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(a) W.R. Wiley Environmental Molecular Sciences Laboratory

(b) Pacific Northwest National Laboratory

Cubic-CeO₂ and α -Fe₂O₃ thin films have been epitaxially grown on yttria-stabilized ZrO₂ and α -Al₂O₃ substrates, respectively, by oxygen-plasma-assisted molecular beam epitaxy. Structural features of the interface between the films and the substrates were characterized by Rutherford Backscattering Spectrometry (RBS), x-ray diffraction, and High-Resolution Transmission Electron Microscopy (HRTEM) (Figure 6). RBS channeling spectra for both CeO₂/ZrO₂ and Fe₂O₃/Al₂O₃ show interface disorder-related scattering peaks believed to be due to interface misfit dislocations. Cross-sectional HRTEM reveals that interfaces of both systems are similarly characterized by coherent regions that are separated by misfit dislocations periodically distributed along the interface. The experimentally observed dislocation spacings are approximately consistent with those calculated from the lattice mismatch, implying that the lattice mismatch is accommodated mainly by interface misfit dislocations.

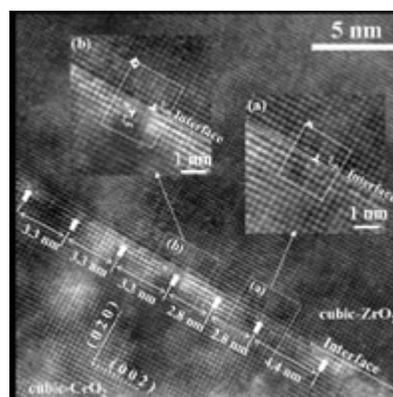


Figure 6. High-resolution transmission electron micrograph of CeO₂(100)/Y-ZrO₂(100).

Awards and Recognition

Dr. Karl Christe, Phillips Air Force Lab, won the American Chemical Society (ACS) Award in Inorganic Chemistry, to be given at the 225th ACS National meeting in New Orleans this spring. Work that Karl did at EMSL is specifically mentioned in the award article in Chemical & Engineering News.

Dr. Fritz Schaefer, University of Georgia, Athens, won the 2003 ACS Award in Theoretical Chemistry, to be given at the 225th ACS National meeting in New Orleans this spring.

Mr. Jason D. Thompson, University of Minnesota, Twin Cities, won the 2001 Midwest Theoretical Chemistry Conference Dirac Award for Outstanding Graduate Research in Theoretical Chemistry for his paper entitled "Reactions of Hydroxide with Chlorinated Hydrocarbons." This paper is associated with his research conducted on EMSL's Molecular Science Computing Facility Grand Challenge, "Chemical Fate of Contaminants in the Environment: Chlorinated Hydrocarbons in the Groundwater."

Russ Tonkyn and Steve Barlow were members of a larger team (Darrell Herling, Christopher Aardahl, Kenneth Rappe, Gary Maupin, Charles H.F. Peden, John Frye, Monty Smith, Delbert Lessor, Jud Virden, and Robert Silva) who won the Federal Laboratory Consortium (FLC) award for the "Engine Exhaust Aftertreatment System Based on Non-Thermal Plasma-Assisted Catalysis." The FLC recognizes outstanding work in accomplishing technology transfer from the national labs to the public and private sectors.

Major Facility Upgrades

Environmental Spectroscopy & Biogeochemistry Facility

\$18K was spent to upgrade the Linux cluster computer, "Seattle," adding six more nodes (12 processors). This upgrade increased the number of processors on Seattle by 85% (from 14 original CPUs to 26). The nodes have been installed and are currently operational. This upgrade will allow a higher throughput for calculations by and for Eric Bylaska's and Kevin Rosso's EMSL users and also improve throughput for their collaborative efforts.

Capital funds are being used to design and build a dual-energy gamma radiation system. The dual-energy gamma radiation system will be used to nondestructively and nonintrusively determine fluid saturations, porous medium bulk density, porosity, and salt concentration values. The major components of the gamma system have been constructed and installed, and the intermediate-scale flow cell has been completed and leak tested. The Instrument Development Laboratory completed about 80% of the motion control system hardware. PNNL Radiation Protection staff completed the design of the radiation shielding for the sealed gamma sources. The shield material has been ordered and will be shipped March 21. In spring 2003, the radiation shield will be complete and the sealed source ordered. The

complete system will then be tested, incorporating the motion control, gamma spectroscopy system, and intermediate-scale flow cell.

Interfacial & Nanoscale Science Facility

In the sputter deposition laboratory, sample-heating capabilities were added in the RF, DC and plasma deposition chambers. A new version of imaging software was added to the electron microscopy suite for better image analysis and file manipulation.

Molecular Science Computing Facility

Phase1 of the Hewlett Packard (HP) supercomputer continues to be in full operation within the Molecular Science Computing Facility (MSCF). Phase1 (Figure 7) consists of 256 Intel Itanium2 processors and 1.5 terabytes of memory. The system has had no unplanned outages, and 99.65% of the resources were available during February. The utilization for this period was 78.2%, the highest rate since becoming operational in December 2002. Delivery of the Phase2a system (6 teraflops) began in February 2003. The system is targeted to become operational by the end of the fiscal year, with early science runs commencing in June 2003.



Figure 7. Phase1 of the HP super-computer.

The operations group continues to make progress on the stabilization and testing of the Lustre filesystem. Lustre is an open-source, object-based, distributed filesystem that will be used on the Phase2 supercomputer and the next-generation EMSL Archive. It uses object-based disks for storage and metadata servers for storing file system metadata. This design provides a substantially more efficient division of labor between computing and storage resources. Replicated, failover metadata servers maintain a transactional record of high-level files and file system changes. Distributed Object Storage Targets are responsible for actual file system I/O and for interfacing with storage devices. This division of labor and responsibility leads to a truly scalable filesystem and more reliable recoverability from failure conditions by providing a unique combination of the advantages of journaling and distributed file systems.

News Coverage

Molecular Science Computing Facility

Scott Studham is quoted in a story on Intels' new Madison/Deerfield processors in Information Week's February 24, 2003, issue (<http://www.informationweek.com/story/IWK20030221S0041>).

The new supercomputer was mentioned in a press release that HP distributed on its smart cooling system (http://biz.yahoo.com/bw/030304/45282_1.html), leading to coverage in

- ZDNet (<http://news.zdnet.co.uk/story/0,,t278-s2131455,00.html>)
- IDGNewsWorld
(<http://www.itworldcanada.com/dailyITWire/viewArticle.cfm?v=5510FBC9-AEEB-499E-BAA3E2BFA6E0FFB2>)
- BioIT World (http://www.bio-itworld.com/news/030503_report2112.html)
- ITWorld.com
(<http://www.windowstechedge.com/Net/3138/030305hpdatacenter/>)
- NetworkWorldFusion.com (<http://nwfusion.com/news/2003/0304hpplans.html>)
- asia.internetnews.com
(<http://siliconvalley.internet.com/news/article.php/2034141>)
- infoworld (http://www.infoworld.com/article/03/03/04/HNhpcool_1.html).

Finally, Platform Computing distributed a press release (<http://www.platform.com/newsevents/pressreleases/prelease.asp?id=55>) on its role in the HP supercomputer for EMSL, leading to a story on GenomeWeb.com (<http://www.genomeweb.com/articles/view-article.asp?Article=20033313839>).

Visitors and Users

Chemistry & Physics of Complex Systems

- Geoffrey Duxbury, University of Strathclyde, Glasgow, Scotland
- Kevin Kittilstved, University of Washington, Seattle
- George Nieman, Monmouth College, Monmouth, Illinois
- Steven Tait, University of Washington, Seattle
- Lai-Sheng Wang, Washington State University, Richland

Environmental Spectroscopy & Biogeochemistry Facility

- Thomas Borch, Montana State University, Bozeman
 - Anna Cavinato and her students, Eastern Oregon University, La Grande
-

High Field Magnetic Resonance Facility

- Elisar Barbar, Ohio University, Athens
- Klara Briknarova, The Burnham Institute, La Jolla, California
- Kathryn Ely, The Burnham Institute, La Jolla, California
- Philip Gee, Oxford Instruments, Hawthorne, New York
- Peter Hogg, Oxford Instruments, Hawthorne, New York
- Mark Hook, Beckwith & Kuffel, Washington
- Stefan Hunger, University of Delaware, Newark
- Evan Kantrowitz, Boston College
- Maksymilian Kozyrczak, Linde Process Plants, Inc.
- Mara Kreishman-Deitrick, University of Texas Southwestern Medical Center, Dallas
- Thomas Leeper, University of Washington, Seattle
- Robert Mantz, Air Force Research Laboratory, Ohio
- Michael Rosen, University of Texas Southwestern Medical Center, Dallas
- Louis Silks, Los Alamos National Laboratory, New Mexico
- Gabriele Varani, University of Washington, Seattle
- Li-Qiong Wang, Pacific Northwest National Laboratory
- David Wemmer, University of California, Berkeley

High Performance Mass Spectrometry Facility

- David Gibb Camp, Pacific Northwest National Laboratory
- Steven P. Gross, University of California, Irvine
- Dave Kimmell, ABB Inc.
- Joel E. Martinez, University of California, Irvine
- Noah K. Rosenberg, Whitman College, Walla Walla, Washington
- Amy K. Schmid, University of Washington, Seattle
- Paul H. Yancey, Whitman College, Walla Walla, Washington
- Xiaohua Yang, State University of New York, Stony Brook

Interfacial & Nanoscale Science Facility

- Andraeus Blutke, Thermal Conversions Corp.
 - Michael Brewer, Micromeritics
 - Michael Donley, Wright Patterson Air Force Base, Ohio
 - Heather Edberg, Innovateck, Inc.
 - Gary Hansen, University of Washington, Seattle
 - Charles Hibbitts, University of Washington, Seattle
 - Randy Perry, University of Washington, Seattle
 - Tran Phung, University of Oregon, Eugene
 - Rajesh Sani, Washington State University, Seattle
 - Richard Smith, Montana State University, Bozeman
-

Molecular Science Computing Facility

- Kennewick School District students, Kennewick, Washington
- Mary McBride, Office of U.S. Senator Patty Murray, Washington
- Lawrence Pratt, Fisk University, Nashville, Tennessee
- National Security Directorate visitors, Pacific Northwest National Laboratory

Molecular Sciences Software - New user agreements with NWChem/Ecce:

- Paul Ayers, McMaster University, Hamilton, Ontario Canada
- Brian W. Beck, University of Nevada, Reno, Nevada
- Alessandro Bencini, University of Florence, Sesto, Italy
- John Bentley, University of Notre Dame, Notre Dame, Indiana
- Rishikesh Bharadwaj, Avery Research Center, Pasadena, California
- Lennane Michel Fonseca-Espinoza, Superior School of Medicine, Mexico City, Mexico
- Paul Kogerler, Ames Laboratory, Iowa State University, Ames, Iowa
- Lawrence Liew, Singapore Computer Systems, Republic of Singapore
- Stephen P. Molnar, Upper Arlington, Ohio
- Arnaud Philippi, Chemistry of Coordination Lab, Tovlovsé, France
- Jose R. Sabino, Sao Carlos, SP, Brazil
- Rochus Schmid, University of Bochum, Germany
- Mateo Valero, Barcelona, Spain
- James Vollmer, Knolls Atomic Power Laboratory, Schenectady, New York

New Facility Staff

Environmental Spectroscopy & Biogeochemistry Facility

- Jon Barr, MS in Mechanical Engineering, Washington University, St. Louis, Missouri
- Janae Strickland, BS Zoology, University of Washington, Seattle, Washington

Molecular Science Computing Facility

- Cynthia Marasco, Senior Research Scientist I
 - Ryan Mooney, Senior Research Scientist II
 - Kevin Mote, College Student
 - Kenneth Schmidt, College Student
-

Publications

Autrey T, S Egerev, NS Foster, A Fokin, and O Ovchinnikov. 2003. "Counting Particles by Means of Optoacoustics: Potential Limits in Real Solutions." *Review of Scientific Instruments* 74(1):628-631.

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