William R. Wiley

EMSL

Environmental Molecular Sciences Laboratory

EMSL Report

March/April 2005

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

Monte Carlo Simulation of the Spatial Distribution of Energy Deposition for an Electron Microbeam

DJ Lynch,[a] WE Wilson,[a] MT Batdorf,[a] MB Sowa,[b] GA Kimmel,[b] and JH Miller[a]
(a) Washington State University Tri-Cities, Richland, Washington
(b) Pacific Northwest National Laboratory, Richland, Washington

This research compares experimental measurements with Monte Carlo models that are used to understand the effects of radiation on biological cells.

Most human exposures to ionizing radiation involve high-energy photons that generate secondary electrons with a broad energy spectrum. These energetic electrons cause a number of lower-energy interactions, distributing energy, for instance, by ionization and excitation in the surrounding medium. Recent experiments with a low-linear energy transfer (LET) microbeam probe suggest that the amount of energy and quality of radiation absorbed by hit cells can also affect neighboring bystander cells. Demonstration of bystander effects induced by low-LET radiation has proven to be more difficult than with high-LET particles. The current study compares experimental spatial distributions of energy deposition for an electron track in air obtained with EMSL's electron microbeam with computed results obtained from Monte Carlo simulation of electron track structures in water, taking into account the relative density of air and water. EMSL's electron microbeam in-air data provide a rare opportunity to test Monte Carlo electron-track simulation codes by comparison with experiments. If agreement is obtained with these physical measurements of electron microbeam characteristics, then we

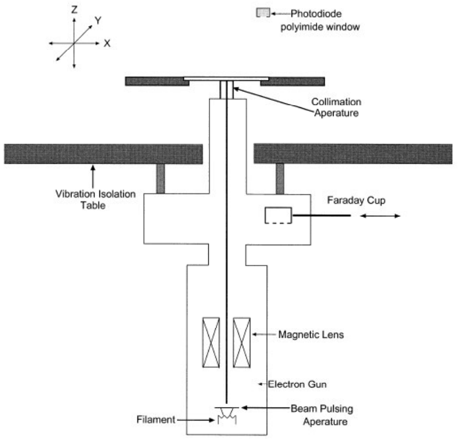


Figure 1. Schematic of EMSL's electron microbeam system.

have greater confidence in the predictions of the track-structure simulations for application of the instrument as a single-cell irradiator.

Figure 1 shows a schematic drawing of the electron microbeam apparatus, as configured for this study. To obtain detailed dosimetry for the electron microbeam, a photodiode was used to measure and characterize the spatial distribution of the microbeam in air, with electron microbeam energies ranging from 25 to 80 keV.

Figure 2 shows a comparison of experimental and computed beam spread, in terms of the full width at half maximum (FWHM) value, as a function of the penetration distance, z, for a microbeam energy of 30 keV. Overall, the agreement between the results of the microbeam in-air experiment and the Monte Carlo simulation of electron tracks in water, scaled by the relative density of the medium, is good. At low penetration, the experimental values of FWHM are slightly greater than predicted by the simulation, and the discrepancy increases for the higher microbeam energies where the beam diameter is smaller. These differences between the simulation and experiment could be due to electron beam scattering within the collimator, which is not included in the simulation model.

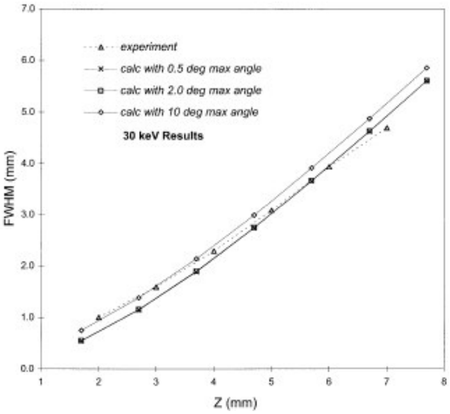


Figure 2. Comparison of experimental and computed values of the FWHM for the energy deposition of a 30-keV microbeam source for a range of penetration distances.

Dosimetry calculations characterizing the spatial variation of the energy deposited by the slowing and stopping of energetic electrons were conducted and compared with experimental measurements. The computations involve event-by-event, detailed Monte Carlo simulations of low-energy electrons interacting in water vapor. Simulations of electron tracks with starting energies of 30 to 80 keV are used to determine energy deposition distributions in thin cylindrical rings as a function of penetration and radial distance from a beam source. Overall, the experimental measurements of the spatial distribution of an electron microbeam in air show general agreement with the density-scaled simulation results for water vapor at these energies, yielding increased confidence in the predictions of Monte Carlo track-structure simulations for applications of the microbeam as a single-cell irradiator. While further experiments would be required to understand and resolve the differences in the observed and computed integrated signal results, the observed level of agreement supports the validity of our dosimetry computation based on a Monte Carlo simulation method. Details of this exiting research are published in Lynch et al. 2005.

Reference

Lynch DJ, WE Wilson, MT Batdorf, MB Sowa Resat, GA Kimmel, and JH Miller. 2005. "Monte Carlo Simulation of the Spatial Distribution of Energy Deposition for an Electron Microbeam." *Radiation Research* 163(4):468-472.

Magnetic Resonance Imaging of Respiratory Structure and Function in Laboratory Animals

KR Minard,[a] R Corley,[a] C Timchalk,[a] HE Trease,[a] LL Trease,[a] R Jacob,[a] DR Einstein,[a] CG Plopper,[b] JR Harkema,[c] TH Robertson,[d] and B Saam[e]

- (a) Pacific Northwest National Laboratory, Richland, Washington
- (b) University of California, Davis, California
- (c) Michigan State University, East Lansing, Michigan
- (d) University of Washington, Seattle, Washington
- (e) University of Utah, Salt Lake City, Utah

State-of-the-art magnetic resonance imaging methods are currently being developed for quantifying respiratory structure and function in laboratory animals, with the goal of developing better models for extrapolating potential human health hazards from animal testing data.

During toxicology testing, laboratory animals are widely employed as human surrogates to assess the potential health risks associated with inhaled pollutants. However, significant differences in respiratory structure and function complicate the determination of human health risks from animal tests. One important factor that ultimately affects the fate of inhaled pollutants is the architecture of respiratory airways. Consequently, detailed descriptions of the three-dimensional airways in laboratory animals must be compiled before better computational methods can be developed to extrapolate human health risks from animal testing data. In recognition of this fact, scientists at EMSL's High-Field Magnetic Resonance Facility have been working closely with users from across the nation to develop high-resolution magnetic resonance imaging methods for visualizing excised respiratory tissue and airway casts. Airway structures are then digitally segmented from magnetic resonance imaging data to reveal detailed three-dimensional models of airway architecture (Figure 3; Timchalk et al. 2001).

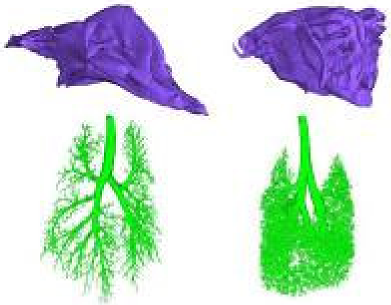


Figure 3. Montage of three-dimensional airway structures. Purple shows nasal sinuses of a monkey and rat on the left and right, respectively. Green shows pulmonary airways for each species.

Major differences in airflow dynamics between animals and humans may further complicate development of predictive models; however, noninvasive methods for

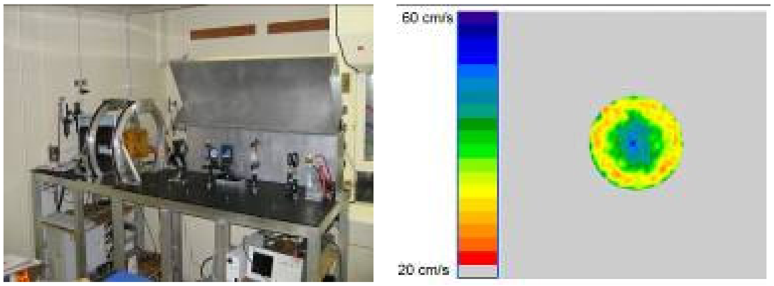


Figure 4. (Left) Optical pumping system for hyperpolarizing ^{3}He gas. (Right) MR imaging map of ^{3}He gas flow in a straight glass tube with a 3.4 mm diameter. Slice thickness is 6 mm and planar resolution is 156 microns. The calibrated color scale shows how flow velocity varies across the tube.

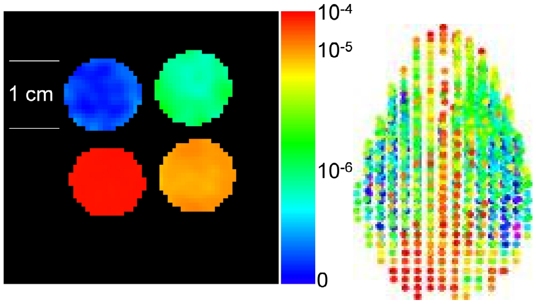


Figure 5. (Left) ^{3}He MR imaging map of regional particle deposition in a foam model of alveolar airways. Four pieces of foam are shown and each was loaded with a different volume fraction of 2-micron-diameter magnetic particles in gas-filled voids. The colorized scale shows the measured volume fraction of magnetic particles and results agree within 15% of known values. (Right) 3D color map of particle deposition in the rat lung measured using fluorescent microspheres and a cryomicrotoming approach. The color scale is different and the lung is viewed front-on from the abdominal side.

visualizing airflow in living animals do not currently exist. To overcome this problem, EMSL scientists worked with collaborators at the University of Utah to develop a unique optical pumping system for hyperpolarizing inert ^{3}He gas. In practice, this system establishes a highly non-equilibrium state characterized by dramatic polarization of the spin-1/2 nucleus of ^{3}He. As a direct result of this so-called hyperpolarized state, ^{3}He gas can be visualized directly with magnetic imaging. At the High-Field Magnetic Resonance Facility, techniques are being developed to image the flow velocity of ^{3}He gas in airway models, so that the dynamics of respiratory airflow can be clearly elucidated with experimental methods (Figure 4). Ultimately, it is envisioned that such imaging technology will provide a quantitative basis for validating computational fluid dynamics predictions to then be used for understanding how risk assessment is influenced by cross-species differences in airflow.

As computer models become more sophisticated, new experimental methods will ultimately be required for their validation. For example, simulations based on airways shown in Figure 4 are capable of predicting the fate of individual particles. Current experimental techniques, however, lack comparable precision. EMSL scientists have developed a new noninvasive magnetic resonance imaging method that exploits the interaction of ^{3}He gas with magnetic particles, allowing researchers to detect both their location and amount. Remarkably, initial tests in model systems indicate that this novel approach may be sensitive enough to detect single magnetic particles in the respiratory tract of a live rat (Minard et al. 2005). Current efforts to validate this technique have benefited from the expertise of researchers at the University of Washington, who specialize in the use of cryomicrotoming for visualizing the deposition of fluorescent microspheres in excised lungs. By exploiting microspheres that are both magnetic and fluorescent, future experiments will examine the correlation between in-vivo magnetic particle detection measured with ^{3}He gas magnetic resonance imaging and fluorescent analysis performed after sacrifice (Figure 5).

References

Minard KR, C Timchalk, and RA Corley. 2005. “T_2-Shortening of ^{3}He Gas by Magnetic Microspheres.” *Journal of Magnetic Resonance* 173(1):90-96.

Timchalk C, HE Trease, LL Trease, KR Minard, and RA Corley. 2001. “Potential Technology for Studying Dosimetry and Response to Airborne Chemical and Biological Pollutants.” *Toxicology and Industrial Health* 17(5-10):270-276.

Cleanup of Environment Using Iron Nanoparticles

DR Baer,[a] EJ Bylaska,[a] KH Pecher,[a] JE Amonette,[a] BD Kay,[a] M Dupuis,[a] JC Linelon,[a] DW Matson,[a] RL Penn,[b] MD Drissen,[b] PG Tratnyek,[c] JT Nurmi,[c] V Sarathy,[c] MH Engelhard,[d] and C Wang[d]
(a) Pacific Northwest National Laboratory, Richland, Washington
(b) University of Minnesota, Minneapolis, Minnesota
(c) Oregon Health and Science University, Portland, Oregon
(d) W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington

Work resulting from a collaboration involving PNNL, Oregon Health and Science University, and the University of Minnesota has shown that some types of iron nanoparticles reduce carbon tetrachloride contamination in water in a more environmentally benign way than larger iron particles or other iron nanoparticles.

The use of nanosized particles of iron for cleaning up contaminants in groundwater, soil, and sediments is an exciting new technology contributing to general enthusiasm about nanotechnology. However, there are a lot of unanswered questions about the appropriate and optimal implementation of the nano-iron technology. Researchers from PNNL, in collaboration with Oregon Health and Science University and the University of Minnesota, have been working during the last few years to understand and exploit the chemical properties of iron nanoparticles (Borchardt 2005, Nurmi et al. 2005). In this research, systematic chemical reaction experiments with nanoparticles have identified some characteristics of nanosized iron particles that may enhance their ability to remove carbon tetrachloride contamination in groundwater.

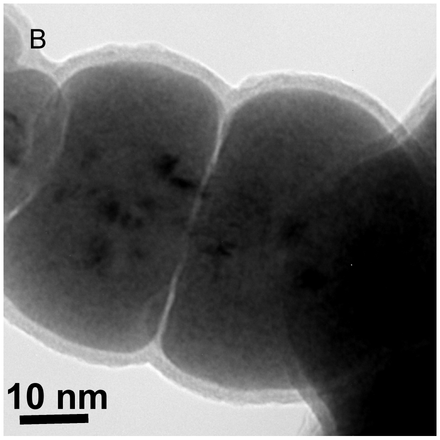


Figure 6. High-resolution transmission electron microscopy image showing the nature of the "protecting" layer on a metallic iron nanoparticle.

Carbon tetrachloride is a manufactured toxic chemical historically used in cleaning fluids, as a degreasing agent, and as part of chemical processing. In many locations around the world, industrial waste and spilled liquids have infiltrated the soil and created very large areas of contaminated groundwater and soil.

Our interdisciplinary team includes 10 researchers from PNNL, three from Oregon Health and Science University, and two from the University of Minnesota. The PNNL researchers have synthesized and characterized several different iron nanoparticles using a variety of advanced microscopy and spectroscopy techniques at EMSL. Chemical reactivity experiments were carried out both at PNNL and Oregon Health and Science University using electrochemical techniques.

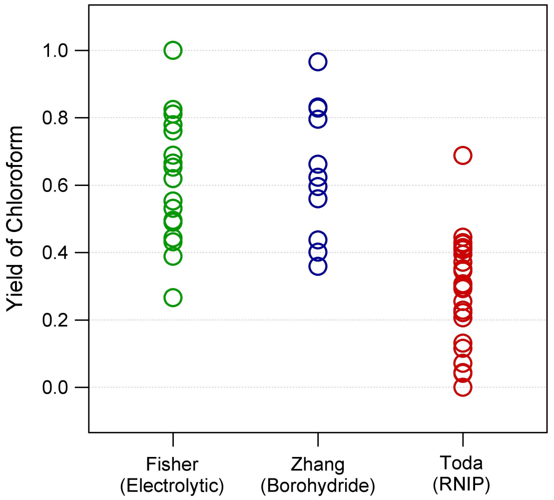


Figure 7. Yield of chloroform versus type of iron nanoparticles. Low chloroform yield suggests two-electron reaction pathway products: CO, etc. Chloroform yield is typically 60 to 80 percent with iron, but one type of nano-iron yields < 0.5. The yield likely is controlled by the composition of the oxide shell.

Several reports indicate that nanosized zero-valent iron (Fe0) exhibits greater reactivity than micron-sized particles of Fe0, which would impart advantages for groundwater remediation or other environmental applications. Most of these comparisons were preliminary in that many potentially significant process variables, including the nature of the particles involved, were either uncontrolled or unresolved. To better understand the reactivity of these iron particles, we collected a range of iron nanoparticles with different size and processing history. Because different synthesis, processing, and handling methods produce nanoparticles of various size distributions, with a variety of surface coatings and contaminants, the nanoparticles may have a significant range of chemical behaviors and reaction properties. Our research focused on measurements of the physical and chemical properties of two materials that have been tested at environmental remediation sites. These iron nanoparticles included single crystal nanoparticles and aggregates of nanoparticles. The particles studied ranged in size from 10 to 100 nm, with the particles coated by an iron-oxide layer of a typical thickness of 2 to 3 nm or a coating rich in oxidized boron (Figure 6) resulting from the synthesis process. Although the reaction rates of the two nanoparticles were similar, the reaction products were significantly different. A commercially produced nanoparticle material that contained both metal particles with a crystalline oxide coating along with fully oxidized nanoparticles degraded carbon tetrachloride to a mixture of relatively harmless products, while larger-sized iron particles and those with boron-rich coatings produced significant amounts of chloroform, an undesirable and toxic by-product (Figure 7).

References

Borchardt, JK. February 10, 2005. “Small Science May Clean a Big Problem.” *Christian Science Monitor*, http://www.csmonitor.com/2005/0210/p14s01-sten.html.

Borchardt, JK. February 10, 2005. “Nanotech Shows Promise for Cheaper Superfund Cleanup.” *USA Today*, http://www.usatoday.com:80/tech/news/nano/2005-02-10-nano-iron-cleanup_x.htm.

Nurmi JT, PG Tratnyek, V. Sarathy, DR Baer, JE Amonette, K Pecher, C Wang, JC Linehan, DW Matson, RL Penn, and MD Driessen. 2005. “Characterization and Properties of Metallic Iron Nanoparticles: Spectroscopy, Electrochemistry, and Kinetics.” *Environmental Science and Technology* 39(5):1221-1230.

Nanostructures for Enzyme Structures

J Kim,[a] JH Kwak,[a] JW Grate,[a] AS Lea,[b] C Wang,[b] J Lee,[c] CW Lee,[c] KS Min,[c] HB Na,[c] HK Ahn,[d] and BS Kim[d]

(a) Pacific Northwest National Laboratory, Richland, Washington
(b) W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington
(c) Seoul National University, Seoul, South Korea
(d) Chungbuk National University, Chongju, South Korea

Enzymes are useful biocatalysts of nanometer scale that regulate the chemistry of cells and organisms. The potential application of enzymes as practical biocatalysts is well recognized and also growing. The unique activities and specificities of enzymes play a key role in yielding the wide range of applications. However, the widespread application of enzymes is generally limited by their short lifetimes. We have developed various nanostructures that can be used to stabilize enzyme activity for several applications.

The first unique nanostructure is "single enzyme nanoparticles." We have developed a new nanostructure containing an enzyme within a hybrid organic/inorganic polymer network with sufficient porosity to allow substrates to diffuse to the active site (Kim and Grate 2003). The synthetic procedure—entailing enzyme modification and two orthogonal polymerization steps—yields nanoparticles containing a single enzyme that can be observed by transmission electron microscopy (Figure 8). In experiments with α-chymotrypsin, incorporation into the nanostructure dramatically increased enzymatic stability. Furthermore, the nanoscale structure around the enzyme is sufficiently thin so that it does not impose a significant mass transfer limitation on the substrate. Because these nanoparticles remain soluble or suspended in solutions, they can be processed into a variety of forms.

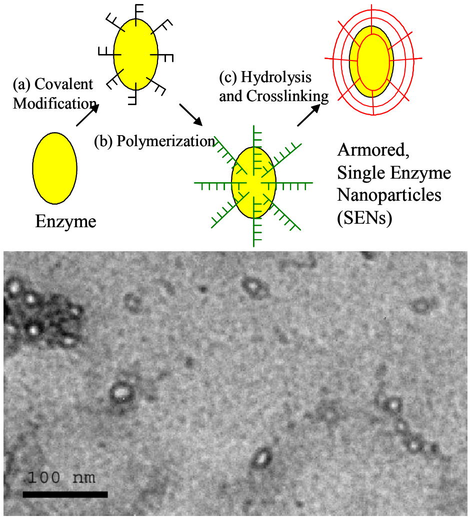


***Figure 8**.* (Top) Schematic of single enzyme nanoparticle synthesis. (Bottom) Transmission electron microscopy images of single-enzyme nanoparticles containing α-chymotrypsin.

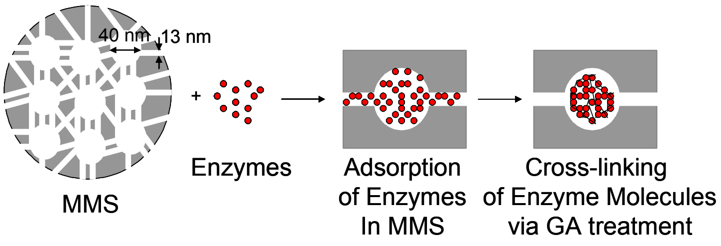


***Figure 9**.* Schematic diagram for nanometer-scale enzyme reactors mesocellular mesoporous silica.

The second nanostructure is mesoporous media (Figure 9). We have developed nanoscale enzyme reactors in mesoporous silica via a ship-in-a-bottle approach, which employs adsorption of enzymes followed by cross-linking using glutaraldehyde treatment. Mesocellular mesoporous silica, small particles (200 to 500 nm) with large mesocellular pores (37 nm) connected by mesoporous channels (13 nm), was selected as a carrier of nanoscale enzyme reactors. The resulting nanoscale enzyme reactors show an impressive stability and activity with an extremely high loading of enzymes. For example, nanoscale enzyme reactors containing α-chymotrypsin could hold 0.5 g of chymotrypsin in 1 g of silica, which is comparable to the maximal loading of chymotrypsin in mesocelluar mesporous silica. However, the specific activity of nanoscale enzyme reactors containing α-chymotrypsin was 4.2 times higher than that of the adsorbed chymotrypsin, with a lower loading (0.07 g of chymotrypsin per 1 g of silica), which was further decreased by a continuous leaching of adsorbed chymotrypsin.

The final nanostructure is electrospun nanofibers. Nanofibers consisting of enzyme-polymer composites have been directly prepared (Figure 10) by electrospinning a toluene solution containing surfactant-stabilized enzyme and polymer.

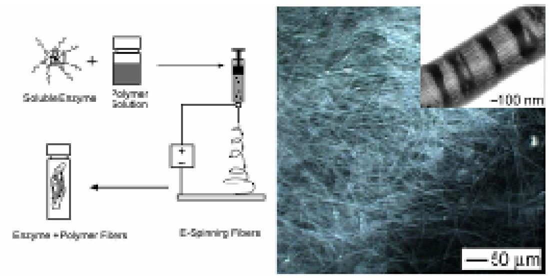


Figure 10. Schematic diagram for the preparation of enzyme-polymer composite nanofibers.

Additional treatment with glutaraldehyde could greatly stabilize the enzyme activity of the fibers, which could be maintained in a buffer under shaking conditions for more than two weeks. The nanofibers also showed great improvement in the enzyme activity over bulk films as a result of increased mass transfer for substrate molecules to and from the enzyme reactive sites. The apparent specific activity of nanofibers with an enzyme loading of 6.3 percent could be achieved up to 40 percent of that of free enzymes. These stable and catalytically active nanofiber-based mats were highly durable and could be easily recovered from a solution, making them ideal candidates for large-scale applications. We have also developed a unique approach for the fabrication of enzyme aggregate coatings on the surfaces of electrospun polymer nanofibers. This approach employs covalent attachment of seed enzymes onto nanofibers consisting of a mixture of polystyrene and poly (styrene-co-maleic) anhydride, followed by a glutaraldehyde treatment that cross-links additional enzyme molecules and aggregates from solution onto the covalently-attached seed enzyme molecules. These cross-linked enzyme aggregates, covalently attached to the nanofibers via the linkers of seed enzyme molecules, are expected to improve the enzyme activity due to increased enzyme loading, and also the enzyme stability.

Reference

Kim JB and JW Grate. 2003. "Single-Enzyme Nanoparticles Armored by a Nanometer-Scale Organic/Inorganic Network." *Nano Letters* 3(9):1219-1222.

Electron Transfer Properties of OmcA, an Outer Membrane Decaheme Cytochrome from the Dissimilatory, Metal-Reducing Bacterium Shewanella oneidensis

NS Wigginton,(a) MF Hochella Jr.,(a) KM Rosso,(b) BH Lower,(b) and L Shi(b)
(a) Virginia Polytechnic Institute and State University, Blacksburg, Virginia
(b) Pacific Northwest National Laboratory, Richland, Washington

Electron transfer reactions at the mineral-microbe interface can significantly control biogeochemical cycling of metals in the environment. These reactions are thought to be mediated by the direct interaction of specific bacterial outer membrane proteins with mineral surfaces. Expanding knowledge of these processes may aid in the development of potential bioremediation strategies for the cleanup of heavy metals and radionuclides.

Cytochromes are enzymes that function in respiration and photosynthesis processes by transferring electrons across a gradient or membrane. Within individual molecules, electrons are shuttled through iron centers in prosthetic heme groups (iron clusters) within the protein framework via a reversible change in oxidation state. Dissimilatory metal-reducing bacteria are hypothesized to use outer membrane cytochromes such as OmcA as primary catalysts for the terminal transfer of electrons into the crystal structure of Fe(III)- and Mn(IV)-oxide mineral surfaces. Using STM and scanning tunneling spectroscopy, this study aims to provide a new understanding of the molecular electron-transfer properties of OmcA, a surface-exposed decaheme cytochrome from the bacterium *Shewanella oneidensis*.

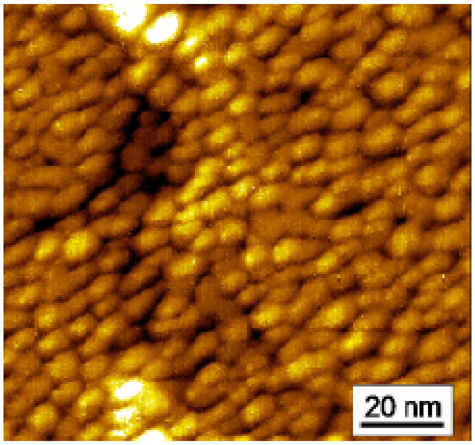
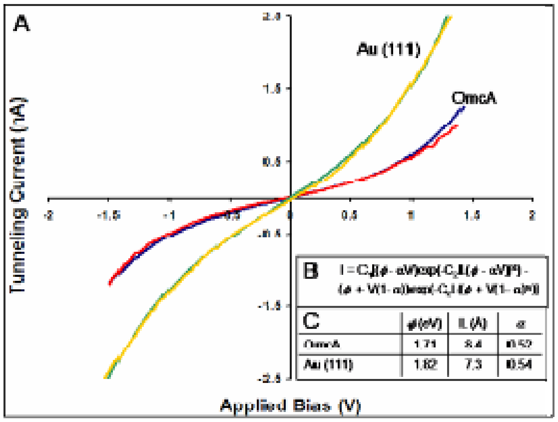


Figure 11. STM image of immobilized OmcA on Au (111) terraces. The uniform size and shape of the cytochrome molecules suggest homogenous distribution and monolayer coverage as well as consistent protein folding. Scan conditions were 1.08 V and 0.5 nA in constant current mode.

OmcA was purified according to previous protocol (Shi et al. 2005). Using a Pico SPM controller and 300S-type scanner (Molecular Imaging Inc.), ambient STM imaging of OmcA–covalently bonded to atomically flat Au (111) films via thiol groups by a tetra-cysteine tag–show a relatively homogeneous monolayer (Figure 11). In some cases, there appears to be a bias-dependent conductivity of the cytochromes, but more work is required to fully describe this phenomenon. Future studies using in situ STM in solution are planned to help to understand these observations. Regardless, stable images in air were collected in constant-current mode over repetitive scans once imaging conditions were optimized.

In addition to imaging, a key component of the STM is that it allows for simultaneous spectroscopic analysis. After the tip is centered over a certain point–in this case, an individual protein molecule–the feedback loop is briefly turned off and the tunneling current (I) is recorded as a function of applied bias voltage (V) swept over a wide voltage range. Several hundred I(V) curves were averaged together over multiple protein molecules on various different protein films [Figure 12(A)]. The averaged data were then fit to a modified Simmons equation for direct tunneling [Zhao et al. 2004; Figure 12(B)] using non-linear regression analysis. Both Au (111) and OmcA tunneling data fit very well to the model, which suggests that direct tunneling is occurring through the cytochromes within the molecular junction. Previously unknown tunneling parameters for OmcA and Au (111) were then projected from the Simmons equation [Figure 12(C)].



$$I = C_1L[(\phi - \alpha V)\exp(-C_2L(\phi - \alpha V)^{½}) - (\phi + V(1-\alpha))\exp(-C_2L(\phi + V(1-\alpha))^{½})]$$

	ϕ(eV)	L(Å)	α
OmcA	1.71	8.4	0.52
Au (111)	1.82	7.3	0.54

Figure 12. (A) Representative experimental I(V) curves for gold (yellow) and OmcA (red) plotted against best-fit curves obtained by non-linear regression analysis. (B) Modified Simmons formula used to model experimental data. (C) Tunneling parameters for gold and OmcA obtained by solving the Simmons formula using the best-fit curves of the experimental data. The parameters are barrier height (ϕ), barrier width (L), and a voltage-ratio parameter (α).

In direct comparison, the difference in barrier height and width between clean Au (111) surfaces and OmcA suggests tunneling between the STM tip and gold was enhanced by the presence of OmcA. Additional studies of other decahemes cytochromes, including MtrA and MtrC, will provide comparable quantitative information specific to different cytochromes in the electron transport chain. With this and other complementary knowledge, in collaboration with EMSL's Biogeochemistry Scientific Grand Challenge, we may have a better understanding of cytochrome-mediated electron transfer reactions that occur at the mineral-microbe interface.

References

Shi L, JT Lin, LM Markillie, TC Squier, and BS Hooker. 2005. "Overexpression of Multi-Heme C-Type Cytochromes." *Biotechniques* 38(2):297-299.

Zhao J, JJ Davis, MSP Sansom, and A Hung. 2004. "Exploring the Electronic and Mechanical Properties of Protein Using Conducting Atomic Force Microscopy." *Journal of the American Chemical Society* 126(17):5601-5609.

Quantitative Proteome Analysis of Beast Cancer Cell Lines

A Patwardhan,[a] MG Pallavicini,[a] EF Strittmatter,[b] DG Camp,[b] RD Smith,[b] and DJ Anderson[c]

(a) University of California, San Francisco, California
(b) Pacific Northwest National Laboratory, Richland Washington
(c) W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington

This research is helping to identify proteins that are changed in breast cancer cells. These changed proteins may be suitable as markers for the detection of breast cancer at an earlier stage, or they may provide a guide for the development of drugs that will attack only the cancer cells.

Breast cancer is the most frequently diagnosed cancer in women and accounts for 30 percent of all cancers diagnosed in the United States. Molecular profiling of proteins that play a role in cancer phenotypes can be studied using high-throughput nucleic acid-based microarrays or through measurements of the cancer cell proteome. However, it is increasingly recognized that transcriptional mechanisms do not always mirror translation, and several labs have shown that nucleic acid-based microarray measurements do not always correlate with protein expression (Harrison et al. 2002). The goal of quantitative proteomics is to produce a list of proteins along with a quantitative measurement, as an amount or concentration, of each of these proteins. Abnormalities in protein expression can contribute to the transformation of a normal cell to a cancer cell; drug-based therapies can be designed to prevent this transformation.

Quantitative proteomics was carried out using a $^{16}O/^{18}O$ stable isotope labeling method where an unnatural isotope of oxygen (having an atomic mass of 18) is incorporated in samples of human mammary epithelial cells. This method is compatible with EMSL's Fourier-transform ion cyclotron resonance (FTICR) mass spectrometers and allows for the determination of relative protein expression measurements of two samples grown under different conditions. The data analysis was performed using the Accurate Mass and Time (AMT) tag database developed at PNNL, requiring ion-trap tandem mass spectrometry identification of two-dimensional liquid chromatography-separated samples. This database provided a total of 2,299 protein identifications, including 514 that were quantified using the AMT tag database and $^{16}O/^{18}O$ method. Eighty-six proteins showed at least a three-fold protein abundance change between cancer and non-cancer cell lines.

Nucleic acid microarray expression data were also available for the same cells studied by quantitative proteomics, and the correlation between the two techniques was of interest to researchers at the University of California, San Francisco and PNNL. Nucleic acid microarray data were available for 70 of the 514 genes already quantified by AMT tag measurements, and consequently, comparison can only be performed using these 70 proteins. When the relative expression of each gene was compared, the correlation between the two sets of values was low ($r^2 = 0.10$). A smaller list of 21 proteins was examined because they showed marked change (at least a three-fold change) in cancer versus normal expression. For 18 of the 21 proteins, nucleic acid microarray and proteome measurements were consistent in that they both indicated overexpression (or underexpression) of a gene product (Table 1). For example, keratin 18 protein should be overexpressed by a factor of 3.42 according to microarray data, whereas proteome measurements also indicate overexpression of this protein, but by a factor of 7.82. These strategies allowed us to compare hundreds of proteins among several cell lines simultaneously and facilitated one of the largest quantitative proteomic studies of breast cancer to date.

Table 1. List of 21 proteins showing at least a three-fold difference in both protein and mRNA Expression between cancer and normal cells (red is > three-fold increase and green is > three-fold decrease relative to normal).

	cancer/normal				
	mRNA	**protein**	**SPN**	**Description**	**cell line**
congruent expression	0.120	0.253	O95573	acyl-CoA synthetase long-chain family member 3	**BT-474**
	0.002	0.269	P00338	lactate dehydrogenase A	
	0.251	0.248	P02570	actin, beta	
	3.420	7.824	P05783	keratin 18	
	0.196	0.310	P14625	tumor rejection antigen 1	
	0.066	0.280	P23526	S-adenosylhomocysteine hydrolase	
	0.321	0.282	P26640	valyl-tRNA synthetase 2	
	0.046	0.258	Q01813	phosphofructokinase, platelet	
	0.001	0.127	P14786	pyruvate kinase	**MDA-231**
	0.191	0.284	P35214	tyrosine 3-monooxygenase activation protein, gamma	
	0.004	0.063	P46940	Ras GTPase-activating-like protein IQGAP1	
	0.018	0.163	P53396	ATP citrate lyase	
	0.217	0.155	Q00765	Polyposis locus protein 1	
	4.592	11.170	P01118	v-Ki-ras2 Kirsten rat sarcoma viral oncogene homolog; Transforming protein p21b	**SKBR-3**
	0.230	0.311	P02570	actin, beta	
	0.024	0.221	P09960	leukotriene A4 hydrolase	
	0.187	0.284	P28288	ATP-binding cassette, sub-family D (ALD), member 3	
	0.002	0.314	P35579	myosin, heavy polypeptide 9	
incongruent expression	41.687	0.291	O00159	myosin IC	**SKBR-3**
	12.445	0.226	P07339	cathepsin D	
	9.226	0.183	P15311	villin 2	

Reference

Harrison PM, A Kumar, N Lang, M Snyder, and M Gerstein. 2002. “A Question of Size: the Eukaryotic Proteome and the Problems in Defining It.” *Nucleic Acids Research* 30(5):1083-1090.

Bacterial Nanowires: A Novel Mechanism for Extracellular Electron Transfer

YA Gorby,[(a)] A Dohnalkova,[(a)] KM Rosso,[(a)] S Yanina,[(a)] AS Beliaev,[(a)] JS McLean,[(a)] and JK Fredrickson[(a)]
(a) Pacific Northwest National Laboratory, Richland, Washington

Metal-reducing bacteria produce electrically conductive appendages (bacterial nanowires) when limited for terminal electron acceptors. This discovery fundamentally transforms our understanding of electron transfer reactions facilitated by bacteria and resulted from combining microscopic and spectroscopic technologies available within EMSL and controlled cultivation technologies available at PNNL' s Microbial Cell Dynamics Laboratory.

Shewanella oneidensis strain MR-1 and other dissimilatory metal-reducing bacteria share the challenge of dealing with reactants and products of respiration that are in the solid phase. While these organisms use a wide range of electron acceptors that are soluble species before and after reduction, they also reduce several metals such as iron or manganese that exist predominantly as oxides or oxyhydroxides. At neutral pH, the solubility of these phases is exceedingly low and the metal ions are poorly available as electron acceptors. We determined that *Shewanella oneidensis* strain MR-1 cells produce extracellular appendages in response to electron acceptor limitation in continuous cultures.

We analyzed *Shewanella oneidensis* MR-1 growing in well-defined continuous cultures (chemostats) with electron acceptor limitation using O_2 as the terminal electron acceptor. Under these conditions, cultures consisted of aggregates of cells with fiber-like appendages ranging from 50 to >150 nm in diameter and as long as tens of microns (Figure 13, left).

These appendages were examined by scanning tunneling microscopy (STM) in air to assess their electrical character. STM is a scanning probe technique that entails detection of a

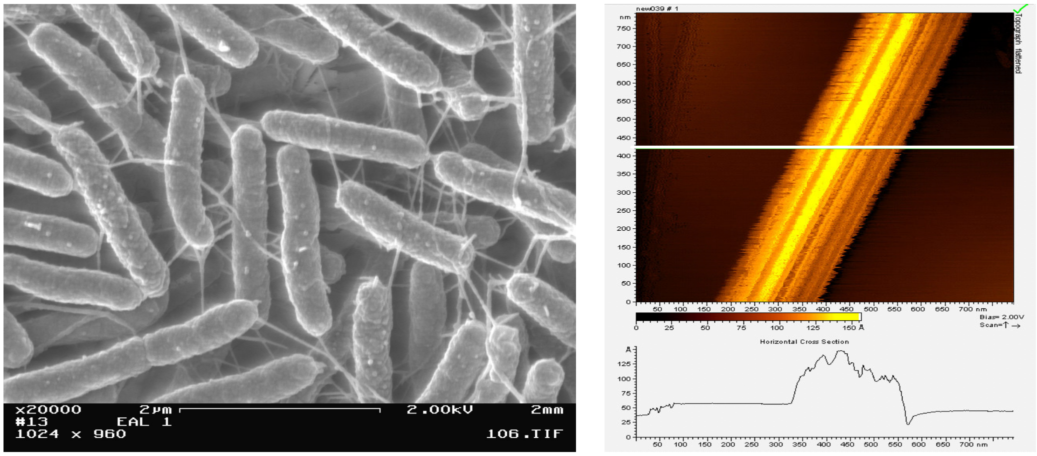


Figure 13. (Left) SEM image of wild-type strain MR-1 taken from an electron acceptor limited chemostat operating at low agitation (50 rpm). (Right) STM image of an isolated appendage from wild-type MR-1, with lateral diameter of 100 nm and a topographic height between 5 and 10 nm. Note ridges and troughs running along the long axis of the structures.

tunneling current passing between a sample electrically biased against an atomically sharp metal tip. For conducting samples, this is a non-contact technique, with tip-sample distances on the order of a few Ångstroms. Appendages from MR-1 cells grown under electron acceptor limitation were applied to a freshly cleaved surface of highly ordered pyrolytic graphite (an STM standard flat conducting substrate) and thoroughly washed with anaerobic solution of phosphate buffered saline followed by anaerobic deionized water to remove salts present in the medium. High-resolution STM images (constant current topographs) of isolated appendages on the graphite surface revealed their widths to range from approximately 5 to 100 nm (Figure 13, right), consistent with dimensions observed by SEM and atomic force microscopy. The apparent heights of the appendages in the STM images were approximately 10 nm (Figure 14, right). At these length scales, height information from STM depends on sample conductivity in addition to actual dimensions. For conducting appendages, the substrate bias voltage is carried from the graphite through the appendage. Hence, the bias voltage drop occurs at the upper surface of the appendage and the tip effectively follows the appendage topography. For poorly conducting appendages, the voltage drop is entirely at the graphite surface; hence, the tip seeks the tunneling current from the graphite alone and is effectively blind to the appendage in between. Intermediate conditions may also exist. In our case, all evidence suggests that these appendages are good electrical conductors.

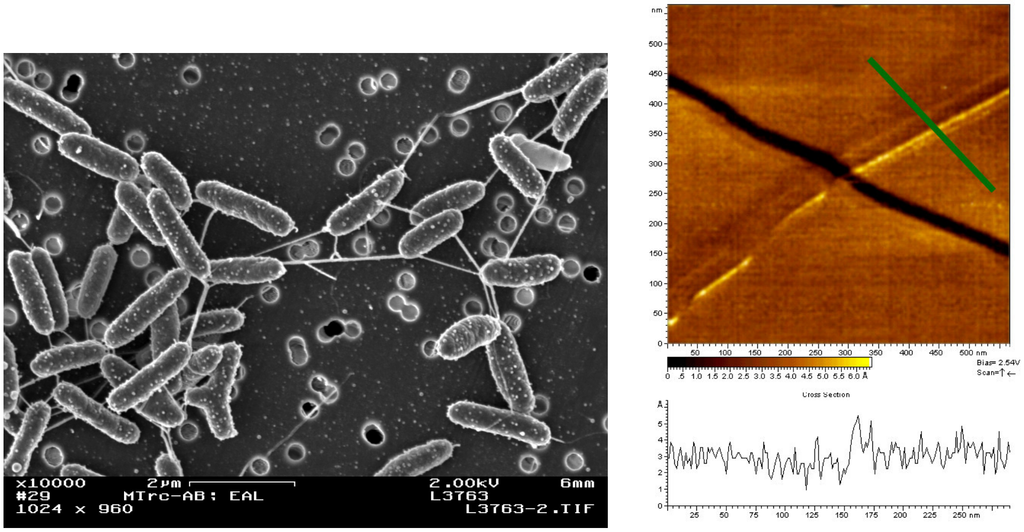


Figure 14. (Left) SEM image of ΔmtrC cultivated under electron acceptor limited conditions. (Right) STM image of nanowire produced by ΔmtrC, revealing a poorly conductive nature of this structure.

We investigated components of bacterial nanowires using mutants rationally chosen from previously published data implicating the role of outer membrane cytochromes in the reduction of iron and manganese oxides. We constructed an in-frame dilution mutant of *mtrC* (*omcB*, SO1778), *⊿mtrC*, which encodes a decaheme c-type cytochrome that has been reported to be localized to the outer membrane and necessary for iron reduction in vivo. SEM revealed that this mutant produced structures (Figure 14, left) with similar physical dimensions as those nanowires produced by wild-type MR-1. However, the STM apparent heights of the ΔmtrC mutant appendages (Figure 14, right) were almost two orders of magnitude less than for the wild-type appendages, indicating that the appendages produced by this mutant were significantly poorer electrical conductors than MR-1. Notably, this mutant, as well as other mutants that formed non-functional nanowires, was unable to reduce solid-phase iron oxides.

Our findings provide important insights into the mechanisms of electron transfer of metal-reducing bacteria to iron and manganese oxides and, perhaps in complex three-dimensional communities such as biofilms.

Controlling the Catalytic Activity of Platinum-Monolayer Electrocatalysts for Oxygen Reduction with Different Substrates

J Zhang,[(a)] MB Vukmirovic,[(a)] Y Xu,[(b)] E Mavrikakis,[(b)] and RR Adzic[(a)]
(a) Brookhaven National Laboratory, Upton, New York
(b) University of Wisconsin, Madison, Wisconsin

Fuel cells provide a promising answer to the world's pressing need for clean and efficient power and play a central role in the "hydrogen-based economy." Investigations of efficient, selective, and less costly electrocatalysts are among the most active fields in fuel cell science and technology. This highlight presents interesting results on controlling the catalytic activity of platinum-monolayer electrocatalysts for oxygen reduction with different substrates.

Oxygen reduction at cathodes is a key step for the electrochemistry processes of fuel cells. Extensive attention has been paid to the searching and fine-tuning of electrocatalysts that are highly efficient and selective toward fuel cell electrode reactions. Currently, platinum metal is widely used as an electrocatalyst for oxygen reduction reactions (ORRs) at fuel cell cathodes because of its high activity and selectivity toward oxygen reduction. However, platinum is a very pricey noble metal material, and alternatives are needed to reduce the cost for practical application of fuel cells.

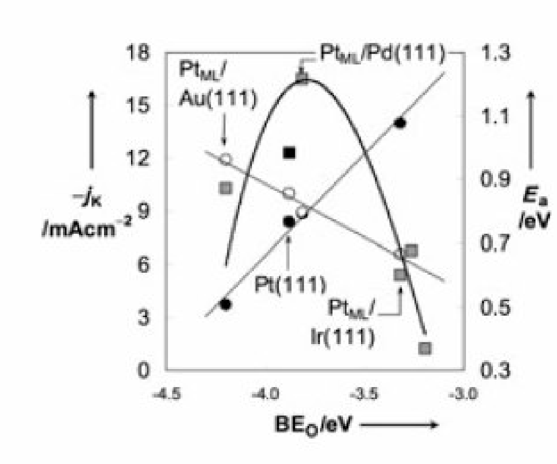


Figure 15. ORR on platinum monolayers exhibits a volcano-type behavior.

Computational and experimental chemists at the University of Wisconsin-Madison and Brookhaven National Laboratory have demonstrated that fuel cells can benefit from coating the cathode with a thin layer of platinum instead of using solid platinum metal. By doing so, the efficiency is raised by 10 percent and the use of expensive platinum can be reduced.

Specifically, electrochemical experiments show that the ORR on platinum monolayers supported on various less expensive transition metals (e.g., gold, palladium, ruthenium, and iridium) exhibits a volcano-type behavior (see Figure 15). These results are in good agreement with predictions from theoretical calculations performed using plane-wave density functional theory. The calculations also reveal that oxygen-oxygen bond-breaking occurs more easily as oxygen-hydrogen bond-making becomes more difficult, and why the palladium-supported platinum monolayer [PtML/Pd(111)] has higher ORR activity than pure Pt(111). These calculations are partially accomplished using EMSL's Molecular Science Computing Facility.

The results elucidate, for the first time, that for a good ORR electrocatalyst, the kinetics of both the oxygen-oxygen bond-breaking and the hydrogenation of reactive intermediates have to be facile at the cathode. More importantly and from a practical perspective, it has been shown that it is possible to devise an ORR electrocatalyst that contains only a fractional amount of platinum but can surpass the activity of pure platinum (e.g., platinum monolayer on Pd(111)). Therefore, platinum monolayers supported on appropriate metal substrates represent a viable way to reduce platinum loadings and the associated cost of fuel-cell electrodes. This study, outlined in Zhang et al. 2005, also points to the fundamentally important possibility of fine-tuning the electrocatalytic activity of transition metals.

This work was highlighted recently in the chemistry web magazine *Reactive Reports* (Bradley 2005).

References

Bradley D. 2005. "Fuel Cells." Reactive Reports #44, March 2005. (http://www.reactivereports.com/44/44_1.html).

Zhang J, MB Vukmirovic, Y Xu, M Mavrikakis, and RR Adzic. 2005. "Controlling the Catalytic Activity of Platinum-Monolayer Electrocatalysts for Oxygen Reduction with Different Substrates." *Angewandte Chemie International Edition* 44(14):2132 –2135.

Reactions of Laser-Ablated Uranium Atoms with H_2O in Excess Argon: A Matrix Infrared and Relativistic DFT Investigation of Uranium Oxyhydrides

B Liang,[a] RD Hunt,[b] GP Kushto,[a] L Andrews,[a] J Li,[c] and BE Bursten[d]
(a) University of Virginia, Charlottesville, Virginia
(b) Oak Ridge National Laboratory, Oak Ridge, Tennessee
(c) W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington
(d) Ohio State University, Columbus, Ohio

The chemistry of uranium, particularly the hydrolysis reaction, is of major importance in the design of nuclear waste repositories and nuclear fuel reprocessing cycles. Uranium reactions with water have been of great interest due to the concerns on the corrosive effect of steam on uranium fuel elements, which is a major safety concern in the operation of nuclear fission reactors. In fact, water is found to act as a catalyst for uranium corrosion in humid air, especially at higher temperatures. This study focuses on the experimental and computational studies of reaction products of laser-ablated uranium atoms with water and a fundamental understanding on the uranium oxo, hydride, and oxyhydride complexes. A series of new uranium species are identified and their structures and vibrational frequencies are assigned.

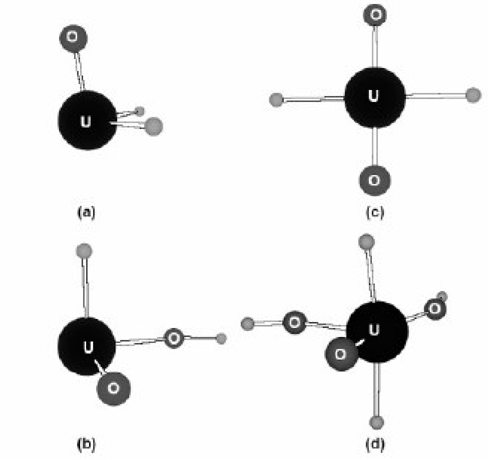


Figure 16. New uranium oxyhydrides, including H_2UO, $HUO(OH)$, H_2UO_2, $H_2U(OH)_3$, are formed.

In this research (Liang et al. 2005), laser-ablated uranium atoms are used to react with H_2O during condensation in excess argon. A series of interesting new uranium oxyhydrides, including H_2UO, $HUO(OH)$, H_2UO_2, $H_2U(OH)_3$ (Figure 16), are formed in these reactions. They are identified through infrared spectroscopy and theoretical calculations based on scalar-relativistic density functional theory. Infrared absorptions at 1416.3, 1377.1, and 859.4 cm^{-1} are assigned to symmetric hydrogen-uranium-hydrogen, antisymmetric hydrogen-uranium-hydrogen, and uranium-oxygen stretching vibrations of the primary reaction product H_2UO. Uranium monoxide, UO, also formed in the reaction, inserts into H_2O to produce $HUO(OH)$, which absorbs at 1370.5, 834.3, and 575.7 cm^{-1}. The $HUO(OH)$ uranium(IV) product undergoes ultraviolet photoisomerization to a more stable H_2UO_2 uranium(VI) molecule, which absorbs at 1406.4 and 885.9 cm^{-1}. Several of these species, particularly H_2UO_2, appear to form weak argon-coordinated complexes based on the calculated uranium-argon distances, binding energies (Figure 17), and the existence of multiple matrix sites, as revealed by the experiments. The predicted vibrational frequencies, relative absorption intensities, and isotopic shifts from relativistic density functional theory calculations are in good agreement with observed spectra, which further support the identification of novel uranium oxyhydrides from matrix infrared spectra.

The reactions of laser-ablated uranium atoms provide interesting similarities and contrasts to those observed for thorium atoms. For oxidation states of +4 or lower, the chemistry of uranium parallels that of thorium in the formation of species such as H_2AnO and HAn(O)OH. This mutual aspect of thorium and uranium chemistry is largely driven by the high oxophilicity of the early actinide elements. The uranium chemistry progresses into oxidation states higher than can be achieved by thorium, especially in the formation of the U(VI) complexes H_2UO_2 and possibly $H_2UO(OH)_2$. Some of the new molecules reported in this work, especially the U(VI) complexes that have uranium in its highest possible oxidation state, may be involved in the oxidation of uranium in aqueous systems, which is an important issue in nuclear waste remediation.

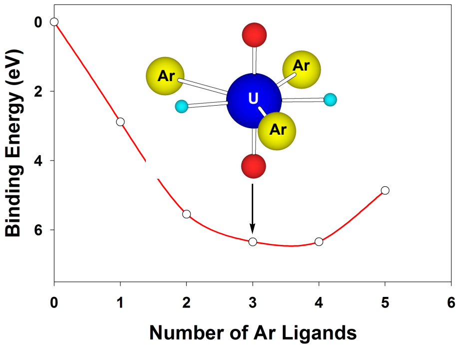


Figure 17. H_2UO_2 appears to form weak argon-coordinated complexes based on the calculated uranium-argon distances, binding energies, and the existence of multiple matrix sites.

These calculations were supported through a heavy-element computational chemistry Grand Challenge project at EMSL and were performed using the 1960-processor Hewlett Packard Itanium2 cluster located in EMSL's Molecular Science Computing Facility.

Reference

Liang B, RD Hunt, GP Kushto, L Andrews, J Li, and BE Bursten. 2005. "Reactions of Laser-Ablated Uranium Atoms with H_2O in Excess Argon: A Matrix Infrared and Relativistic DFT Investigation of Uranium Oxyhydrides." *Inorganic Chemistry* 44(7):2159-2168.

Awards and Recognition

Associate Director Featured as Great Laboratory Manager. Gordon Anderson, EMSL Acting Associate Director, was featured as a “Great Laboratory Manager” in the February 2005 issue of Reed Business Information’s *Laboratory Equipment*. In the issue, Anderson is honored for his leadership of a team that manages data produced by in-house and visiting researchers using fifteen state-of-the-art instruments in EMSL’s High-Performance Mass Spectrometry Facility.

EMSL Director Honored by the American Chemical Society. Allison, Campbell, Director, has been selected by ACS the receive the 2005 Regional Industrial Innovation Award for her work in bioceramic coatings. Under Campbell’s guidance, researchers at PNNL have developed a biomimetic process that addresses the poor interfacial bonding between a metal implant and bone tissue in artificial joint implants, such as hip and knee replacement.

Patent Awards. Richard Weller, Michael Lind, Darrell Fisher, Anna Gutowska, and Allison Campbell received U.S. Patent 6,869,588, "Stimulus sensitive gel with radioisotope and methods of making". Jim Amonette, Tom Autrey, Nancy Foster-Mills, David Green received U.S. Patent 6,873,415, "Photoacoustic spectroscopy sample array vessel and photoacoustic spectroscopy method for using the same".

EMSL User Honored as 2005 Guggenheim Fellow. Lai-Sheng Wang, Washington State University-Tri-Cities, Richland, Washington, was recently honored as a 2005 Guggenheim Fellow by the Guggenheim Foundation. Fellows are appointed on the basis of distinguished achievement in the past and for exceptional promise for future accomplishments. He was selected for this honor for his work in atomic clusters and multiplying charged anions. He also received the 2005 College of Sciences Distinguished Faculty Award from Washington State University for his research at PNNL, leadership in the field of nanoclusters, and pioneering research in the study of multiply charged anions.

Major Facility Upgrades

A Spectra-Physics Nd:YAG-pumped Master Optical Parametric Oscillator laser was moved from PNNL’s 331 Building into EMSL’s Environmental Spectroscopy Laboratory. While this laser belongs to PNNL’s Fundamental Science Directorate’s Chemical Sciences Division, it will be available to EMSL users using the induced-time-resolved fluorescence spectroscopy system, as well as for the development of a laser-induced breakdown spectroscopy capability.

News Coverage

Sticky Ice. PNNL researcher and EMSL user Jim Cowin's research on the chemical and physical properties of atmospheric dust and water ice – or "sticky ice" – was the subject of a PNNL news release issued March 8, 2005. The research has received considerable coverage in newspapers and publications around the region and nation, including MSNBC's news web site, Discovery.com, *The Oregonian* and the *Tri-City Herald.* Cowin and his colleagues, including EMSL researcher Martin Iedema, have been using an array of instruments at EMSL to calculate the stickiness of the ice and their formation of planets. Such sticky ice is observed today in comets, planets, and moons in the solar system.

New EMSL Staff

Brian LaMarche joined the Instrument Development Laboratory on April 1. His role as a software developer is comprised of building instrument control and automation software for researchers within EMSL and across PNNL. Prior to joining the Instrument Development Laboratory, Brian was an intern at PNNL. In December, he obtained his B.S. degree in Computer Science from Washington State University. Brian brings with him an excellent combination of technical knowledge and problem-solving skills

Visiting Users

Chemistry and Physics of Complex Systems Facility

- Olexandr Bondarchuk, University of Texas, Austin, Texas, worked on the study "Atomically Resolved Studies of Transition Metal Oxides."
- Yury Dessiaterik, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, gave the seminar "Probing Composition and Chemistry with Single Particle Mass Spectroscopy."
- Norman Dovichi, University of Washington, Seattle, Washington, gave the seminar "Single Cell Proteomics."
- Demetra Farley, Prairie View A&M University, Prairie View, Texas, worked on the study "Fluorescence Imaging of Cellular Protein Dynamics."
- Carey Johnson, University of Kansas, Lawrence, Kansas, gave the seminar "Single-Molecule Spectroscopy of Calcium Signaling."
- Hee Jung Jung, University of California, Davis, California, gave the seminar "Nanoparticle Surface Chemistry: Kinetics, Visualization and Toxicity."
- Hadi Lioe, University of Melbourne, Parkville, Victoria, Australia, worked on the study "Mechanisms of Fragmentation of Post Translationally Modified Peptides."

- Vladimir Mikheev, Innovatek, Inc., Richland, Washington, worked on the ongoing research collaboration “Ultra-Trace Molecular Detection Instrumentation Based on Aerosol Nucleation with Rapid Preconcentration and Separation.”
- Bill Robertson, University of California, Irvine, California, worked on the study “Laboratory Studies of Atmospheric Processing of Sea Salt.”
- Luis Rodriguez, National Cancer Institute, Bethesda, Maryland, worked on the study “Development of Multi-Functional Microscopy (MFM) for Cancer and AIDS Research.”
- Katsumi Tanimura, Osaka University, Ibaraki, Osaka, Japan, worked on the study “Temperature-Dependent Yield of Frenkel Pairs Generated by Valence Excitation in NaCl.”
- Rahmat Ullah, Texas Tech University, Lubbock, Texas, gave the seminar “Development of Gas Particle Ion Chromatography Systems for Atmospheric Measurements.”
- Zhibo Yang, Wayne State University, Detroit, Michigan, gave the seminar “Experimental and Theoretical Studies of Tautomerization, Modification and Metal Cationization of Nucleic Acid Bases.”
- Tieqiao Zhang, National Institutes of Health, Bethesda, Maryland, worked on the study “Analysis of Lipid Nanoparticle Interaction with Cell Membrane.”

Environmental Spectroscopy and Biogeochemistry Facility

- William P. Ball, Johns Hopkins University, Baltimore, Maryland, along with Chongxuan Liu and Zheming Wang, Pacific Northwest National Laboratory, Richland, Washington, continued their collaboration characterizing aqueous uranyl carbonate species by laser-induced time-resolved fluorescence spectroscopy.
- Saumyaditya Bose, a graduate student from the laboratory of Michael Hochella Jr. at Virginia Polytechnic Institute and State University, (Figure 18) is working with scientists Brian Lower and Yuri Gorby from the Pacific Northwest National Laboratory, Richland, Washington, to examine the reduction kinetics of whole cell electron transfer by *Shewanella oneidensis* to synthetic hematite nanoparticles. As part of EMSL’s Biogeochemistry Scientific Grand Challenge, the overall goal of this work is to understand the effects that surface area and electronic properties have on the reduction kinetics of hematite nanoparticles by *Shewanella oneidensis*.

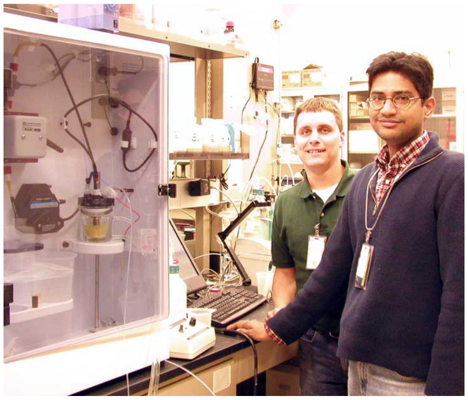


Figure 18. Brian Lower and Saumyaditya Bose.

- Hailiang Dong, Miami University, Oxford, Ohio, and EMSL researcher Ravi Kukkadapu analyzed nontronite clay samples at lower temperatures by Mössbauer spectroscopy to resolve contribution (and relative contents) of various iron sites (tetrahedra and cis- and trans-octahedral). This research will be useful in understanding the biotransformation of nontronite clays that are abundant in soils.

- Daniel Ewert, Pacific Northwest National Laboratory, Sequim, Washington, and Zheming Wang, Pacific Northwest National Laboratory, Richland, Washington, performed fluorescence spectroscopy measurements on a series of fungi samples grown under different aqueous conditions. One goal of this project is to further the basic science that could support the development of novel marine biosensors and enhanced biosentinels to complement existing devices used for biological weapons detection in marine systems. One such biosensor may use fungi that are unique in their ability to function in areas and in ways not addressed by current sensor technologies. The researchers are presently analyzing the fluorescence data, and additional fungi samples and measurements are expected in the near future.

- Jack Istok and Melora Park, Oregon State University, Corvallis, Oregon (Figure 19), along with Mart Oostrom, Pacific Northwest National Laboratory, Richland, Washington, and EMSL scientist Tom Wietsma, have been performing a 12-month-long experiment designed to determine the fate of N_2 gas produced by micro-organisms. Istok and Park visited EMSL to collect sediment samples from their flow cell experiment, which will be analyzed for microbial content. Understanding the fate and transport of nitrogen gas produced in situ is important to evaluating the potential effectiveness of uranium and technetium bioreduction.

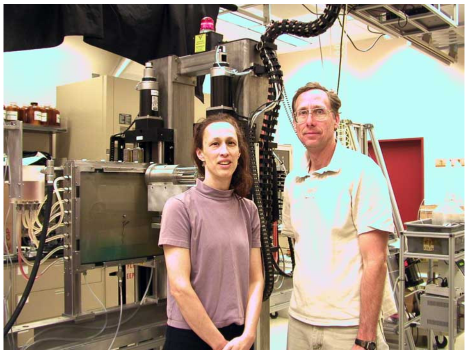


Figure 19. Jack Istok and Melora Park.

- Dan Kaplan, Westinghouse Savannah River, Aiken, South Carolina, and EMSL researcher Ravi Kukkadapu continued Mössbauer measurements of Savannah River sediments to identify the contribution of iron oxides to an iron-poor unsaturated subsurface sediment containing phyllosilicates. The characterization was essential to understand the role of various iron minerals on plutonium mobility during long-term transport in the sediment.

- Mary Neu, Hakim Boukhalfa, and Gary Icopini, Los Alamos National Laboratory, Los Alamos New Mexico, and Alice Dohnalkova, Pacific Northwest National Laboratory, Richland, Washington, conducted transmission electron microscopy imaging and analyses of bacterial cultures of *P. putida*. This ongoing project is focused on reduction of metals and radionuclides such as uranium and plutonium, and their association with bacterial membranes.

- Ken Williams, Lawrence Berkeley National Laboratory and University of California, Berkeley, California, (Figure 20) and Jim Amonette, Pacific Northwest National Laboratory, Richland, Washington, initiated a collaboration to test the geophysical responses (complex resistivity) of oxidized and reduced clays. This measurement approach is being used by Williams to follow bioremediation processes in the subsurface at a field site in Colorado.

Figure 20. Ken Williams.

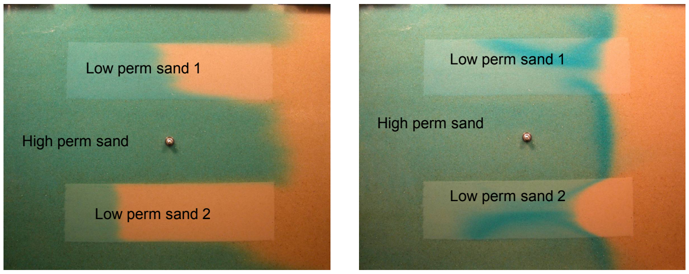


Figure 21. Sweeping efficiency comparison: (Top) A heterogeneous porous media system is flooded with blue-dyed water (at 0.7 PV of flow cell). (Bottom) The same heterogeneous system is flooded with blue-dyed 600 ppm xanthan gum polymer solution with viscosity of 40 cp (at 0.7 PV of flow cell). The sweeping efficiency enhancement attributed to the application of polymer solution is clearly demonstrated.

- Lirong Zhong, Pacific Northwest National Laboratory, along with Mart Oostrom, Pacific Northwest National Laboratory, Richland, Washington, and EMSL scientist Tom Wietsma, is conducting experiments on a heterogeneous packed two-dimensional flow cell to demonstrate the capability of mobility-controlled-flooding in overcoming flow bypassing caused by heterogeneity (Figure 21). Polymer is used to modify the mobility of the fluid so that bypassing is minimized and a complete sweep is achieved in the heterogeneous system. A section of remediation for dense non-aqeous phase liquid is contained in this research to show enhanced subsurface remedial performance with the mobility-controlled-flooding technology.

High-Field Magnetic Resonance Facility

- Cheryl Arrowsmith, University of Toronto (University Health Network), Toronto, Ontario, Canada, sent samples to be run on the 800-MHz, 750-MHZ, and 500-MHz spectrometers for the study “Structural Proteomics: Annotating the Genome Using 3D Structure.”
- Asmeret Berhe, University of California, Berkeley, Berkeley, California, used the 300-MHz spectrometer for the study “Stabilization of Soil Organic Matter: Land Use, Erosion, and Burial.”
- Klara Briknarova, The Burnham Institute, La Jolla, California, sent samples to be run on the 600-MHz and 750-MHz spectrometers for the study “Structure of PR Domain of RIZ1 tumor Suppressor.”
- Peter Brzovic, University of Washington, Seattle, Washington, used the 600-MHz spectrometer for the study “NMR Structural Investigations of BRCA1.”
- Myriam Cotten, Pacific Lutheran University, Tacoma, Washington, sent samples to be run on the 500-MHz spectrometer for the study “Investigating Molecular Recognition and Biological Function at Interfaces Using Antimicrobial Peptides.”
- Leonard Fifield, Pacific Northwest National Laboratory, Richland, Washington, used the 300-MHz and 500-MHz spectrometers for the study “NMR Analysis of Synthesized Organic Compounds for Modification of Nanostructures.”
- Jian Zhi Hu, Pacific Northwest National Laboratory, Richland, Washington, used the 300-MHz spectrometer for the study “In-situ High Field, High Resolution NMR Spectroscopy.”
- Michael Kennedy, Pacific Northwest National Laboratory, Richland, Washington used the 900-MHz, 800-MHz, 750-MHz, 600-MHz, and 500-MHz spectrometers for the

studies “Structural Genomics Collaborative Access Team (CAT)” and “NMR Structural Studies of Clustered DNA Damage.”

- Andrew Lipton, Pacific Northwest National Laboratory, used the 800-MHz and 500-MHz spectrometers for the studies “Correlation of Structure and Function of Zinc Metalloproteins Via Solid-state NMR Methods” and “Investigation of the role of Mg^{2+} in DNA repair proteins APE1, Pol, and FEN1.”
- David Lowry, Pacific Northwest National Laboratory, Richland, Washington, used the 500-MHz spectrometer for the study “Development of Multipurpose Tags and Affinity Reagents for Rapid Isolation and Visualization of Protein Complexes.”
- Asanga Padmaperuma, Pacific Northwest National Laboratory, Richland, Washington, used the 300-MHz spectrometer for the study “Development of Organophosphorus Compounds for Solid-State Lighting Applications.”
- Jennifer Popham, University of Washington, Seattle, Washington, used the 300-MHz spectrometer for “Study of the Binding Mechanism of Mutant SN-15 to Hydroxyapatite Using $^{15}N\{^{31}P\}$REDOR.”
- Ponni Rajagopal, University of Washington, Seattle, Washington, sent samples to be run on the 900-MHz and 800-MHz spectrometers for the study “AlphaB-Crystallin - the Core and the Oligomer: A Structural Investigation.”
- Raymond Reeves, Washington State University, Pullman, Washington, sent samples to be run on the 900-MHz spectrometer for the study “Structural Biology of the Human High Mobility Group A (HMGA) Proteins: Characterizing the Hub of Nuclear Function.”
- Xuefeng Ren, Southern Illinois University, Carbondale, Illinois, used the 600-MHz and 800-MHz spectrometers for “Structural Studies of Lipid-free Apolipoprotein A-I.”
- Thomas Squier, Pacific Northwest National Laboratory, Richland, Washington, used the 500-MHz spectrometer for the study “Development of Multipurpose Tags and Affinity Reagents for Rapid Isolation and Visualization of Protein Complexes.”
- Li-Qiong Wang, Pacific Northwest National Laboratory, Richland, Washington, used the 500-MHz spectrometer for the study “High Resolution NMR Investigation of the Nano-Materials.”
- Marvin Warner, Pacific Northwest National Laboratory, Richland, Washington, used the 500-MHz and 300-MHz spectrometers for the study “Routine ^{1}H and ^{13}C NMR Analysis of Functionalized Semiconductor and Metallic Nanoparticles Synthesized for Biodetection Studies.”

High-Performance Mass Spectrometry Facility

- Josh Adkins, Pacific Northwest National Laboratory, Richland, Washington, is working on the study “Identifying Targets for Therapeutic Interventions using Proteomic Technology.” The PT databases for *Salmonella typhimurium*, *Salmonella typhi*, and the *Vaccinia* virus are being populated, with *S. typhimurium* having the largest database so far. Mutant varieties of *S. typhimurium* are being sent from collaborators at Oregon Health and Science University and will be analyzed to determine which proteins are being up- or down-regulated. *S. typhimurium* cells grown in various eukaryotic cells have also been sent from these collaborators and are being analyzed to further identify target proteins that may lead to identification of virulence factors for this organism.

- Steven Gross University of California, Irvine, California, is working on the study "Determination of the Proteome of Drosophila Lipid Droplets." In collaboration with EMSL, his lab is using a proteomics approach to identify regulators of organelle transport. The focus has been on the comprehensive identification of the factors regulating a single transport process involving lipid droplets from Drosophila embryos.
- Tom Metz, Pacific Northwest National Laboratory, Richland, Washington, is working on the study "Advanced Proteomics and Metabolomics Studies of Type 1 Diabetes." Data from human plasma and human pancreatic islets are being processed to determine the next logical step in this project. At present, the required experiments are roughly half completed, with the second half anticipated to occur during the next two to three weeks.
- Liang Shi, Pacific Northwest National Laboratory, Richland, Washington, is studying a specific host-pathogen interaction between *Salmonella typhimurium* and mouse macrophage cells (with or without a protein known as NRAMP1). In order to study this interaction, Shi is attempting to purify Salmonella-containing vacuoles (SCV) from the macrophages cells and characterize the differing protein complements. The SCV preparations are trypsin digested and analyzed by reversed-phase high-resolution liquid chromatography/tandem mass spectrometry and liquid chromatography/FTICR mass spectrometry. This research is helping to develop a knowledge base for pathogenic *Salmonella* interactions with its host.
- Arzu Umar, Erasmus University Medical Center, Rotterdam, The Netherlands, is visiting EMSL with the goal to characterize functional pathways that lead to clinical resistance to tamoxifen (anti-estrogen) in breast cancer patients; the responsible key proteins will be identified from laser microdissection-based tumor samples using state-of-the-art liquid chromatography/FTICR mass spectrometry. Laser microdissection techniques enable isolation of selected subpopulations of cells, thereby effectively addressing the issue of cell heterogeneity within the tumor; however, the minimal quantity of available sample (less than 5,000 cells corresponding to only a few micrograms of total protein) has seriously limited the ability to perform comprehensive analysis using contemporary proteomics tools. Ultra-sensitive liquid chromatography/FTICR mass spectrometry technology developed at EMSL offers a unique opportunity to study protein profiles within tissue specimens procured by microdissection techniques.

Interfacial and Nanoscale Science Facility

- Zsuzsanna Balogh, Washington State University, Pullman, Washington, used the electron microscopy suite to characterize the mineral nanostructures in order to understand issues associated with soil mineral weathering.
- Sauha Cheung, University of Wisconsin, Milwaukee, Wisconsin, used molecular beam epitaxy to grow a number of thin films of iron oxides on a substrate having polar surface [MgO(111)]. During this same visit, Cheung characterized the films using x-ray photoemission spectroscopy and x-ray diffraction.
- Sarah Huson, Washington State University, Pullman, Washington, used the Zeiss Leo 982 FE-SEM to study the surface texture of zircon grains from the Sierra Madera impact structure in West Texas.
- Kevin Kittilstved, University of Washington, Seattle, Washington, used various analytical and spectroscopic techniques, such as time-of-flight secondary ion mass spectrometry and x-ray photon spectroscopy, to characterize electronic defects (e.g.,

nitrogen, hydrogen, phosphorus) in nanocrystalline ZnO thin films and correlate findings with the observed magnetic properties.

- Madusudan Kongara, Boise State University, Boise, Idaho, used the transmission electron microscopy lab to investigate the microstructural details of powder and thin film samples of oxide semiconductors SnO_2, TiO_2, and ZnO doped with magnetic impurities to produce magnetism.
- Theresa Marie McIntire, University of California, Irvine, California, characterized ozone-oxidized unsaturated self-assembled monolayers using time-of-flight secondary ion mass spectrometry and Auger electron spectroscopy.
- Nicholas Norberg, University of Washington, Seattle, Washington, synthesized and characterized by x-ray diffraction, transmission electron microscopy, and possibly electron paramagnetic resonance spectroscopy a series of nanocrystalline ferromagnetic oxide semiconductor materials of direct relevance to spintronics applications.
- Fumio Ohuchi, University of Washington, Seattle, Washington, discussed research related to the synthesis and characterization of new materials for thermoelectric power generations.

Molecular Sciences Software – New User Agreements with NWChem/Ecce

- Apologetics Press, Inc., Montgomery, Alabama
- Atomic Energy Research Institute, Tokai, Japan
- Belarusian National Technical University, Minsk, Belarus
- Carnegie Mellon University, Pittsburgh, Pennsylvania
- City University of New York, New York, New York
- East Tennessee State University, Johnson City, Tennesee
- Information and Mathematical Science Laboratory, Tokyo, Japan
- Institute of Bioscience, Huddinge, Sweden
- Kent State University, Kent, Ohio
- Khon Kaen University, Khon Kaen, Thailand
- Marian College, Indianapolis, Indiana
- Michigan Technological University, Houghton Michigan
- National Renewable Energy Laboratory, Golden, Colorado
- Northwestern University, Evanston, Illinois
- Technical University of Munich, Garching, Germany
- Tulane University, New Orleans, Louisiana
- Sandia National Laboratories, Albuquerque, New Mexico
- Schlumberger Cambridge Research, Cambridge, Great Britain
- Seoul National University, Seoul, South Korea
- South Dakota State University, Brookings, South Dakota
- SRI International, Menlo Park, California
- State University of New York at Buffalo, Buffalo, New York

- Supercomputing Center of Catalonia (CESCA), Barcelona, Spain
- Syngenta, Bracknell, Great Britain
- Tel Aviv University, Tel Aviv, Israel
- Universidad Autonoma de Mexico, Estado de Mexico, Mexico
- Universita di Bologna, Bologna, Italy
- Universita di Ferrara, Ferrara, Italy
- Universitat Konstanz, Konstanz, Germany
- Universitat Rostock, Rostock, Germany
- University of Alabama, Tuscaloosa, Alabama
- University of Albany, Albany, New York
- University of California, Berkeley, California
- University of Florida, Gainesville, Florida
- University of Graz, Graz, Austria
- University of Nebraska, Lincoln, Nebraska
- University of Podlasie, Siedice, Poland
- University of Rome, Rome Italy
- University of South Florida, St. Petersburg, Florida
- University of Texas-Pan American, Edinburg, Texas
- University of Wales Bangor, Bangor, Great Britain
- Virginia Polytechnic Institute and State University, Blacksburg, Virginia

Publications

The following list represents publications by EMSL staff members and users where the publication resulted from research carried out at EMSL.

Alexandrova AN, AI Boldyrev, HJ Zhai, and LS Wang. 2005. “Photoelectron Spectroscopy and *ab initio* Study of the Doubly Antiaromatic B_6^{2-} Dianion in the LiB_6^- Cluster.” *Journal of Chemical Physics* 122(5):054313, 1-8.

Azad S, OA Marina, CM Wang, LV Saraf, V Shutthanandan, DE McCready, A El-Azab, JE Jaffe, MH Engelhard, CHF Peden, and S Thevuthasan. 2005. "Nanoscale Effects on Ion Conductance of Layer-by-Layer Structures of Gadolinia-Doped Ceria and Zirconia." *Applied Physics Letters* 86(13):131906, 1-3.

Barnard AS, P Zapol, and LA Curtiss. 2005. "Modeling the Morphology and Phase Stability of TiO_2 Nanocrystals in Water." *Journal of Chemical Theory and Computation* 1(1):107-116.

Bouanich JP, C Boulet, A Predoi-Cross, SW Sharpe, RL Sams, MAH Smith, CP Rinsland, DC Benner, and VM Devi. 2005. “A Multispectrum Analysis of the ν_2 Band of $H^{12}C^{14}N$: Part II. Theoretical Calculations of Self-Broadening, Self-Induced Shifts, and Their Temperature Dependences.” *Journal of Molecular Spectroscopy* 231(1):85-95.

Bowman MK, D Becker, MD Sevilla, and JD Zimbrick. 2005. “Track Structure in DNA Irradiated with Heavy Ions.” *Radiation Research* 163(4):447-454.

Buchko GW, K McAteer, SS Wallace, and MA Kennedy. 2005. “Solution-State NMR Investigation of DNA Binding Interactions in *Escherichia coli* Formamidopyrimidine-DNA Glycosylase (Fpg): A Dynamic Description of the DNA/Protein Interface.” *DNA Repair* 4(3):327-339.

Cape JL, MK Bowman, and DM Kramer. 2005. "Reaction Intermediates of Quinol Oxidation in a Photoactivatable System that Mimics Electron Transfer in the Cytochrome bc1 Complex." *Journal of the American Chemical Society* 127(12):4208-4215.

Cape JL, MK Bowman, and DM Kramer. 2005. “Reaction Intermediates of Quinol Oxidation in a Photoactivatable System that Mimics Electron Transfer in the Cytochrome bc1 Complex.” *Journal of the American Chemical Society* 127(12):4208-4215.

Corrales LR, A Chartier, and R Devanathan. 2005. “Excess Kinetic Energy Dissipation in Materials.” *Nuclear Instruments and Methods in Physics Research Section B. Beam Interactions with Materials and Atoms* 228(1-4):274-281.

Devanathan R, LR Corrales, WJ Weber, A Chartier, and C Meis. 2005. “Molecular Dynamics Simulation of Defect Production in Collision Cascades in Zircon.” *Nuclear Instruments and Methods in Physics Research Section B. Beam Interactions with Materials and Atoms* 228(1-4):299-303.

Devi VM, DC Benner, MAH Smith, CP Rinsland, A Predoi-Cross, SW Sharpe, RL Sams, C Boulet, and JP Bouanich. 2005. "A Multispectrum Analysis of the ν_2 Band of $H^{12}C^{14}N$: Part I. Intensities, Broadening, and Shift Coefficients." *Journal of Molecular Spectroscopy* 231(1):66-84.

Disselkamp RS, TR Hart, AM Williams, JF White, and CHF Peden. 2005. "Ultrasound-Assisted Hydrogenation of Cinnamaldehyde." *Ultrasonics Sonochemistry* 12(4):319-324.

Fanourgakis GS, E Apra, WA de Jong, and SS Xantheas. 2005. "High-level *ab-initio* Calculations for the Four Low-Lying Families of Minima of $(H_2O)_{20}$: II. Spectroscopic Signatures of the Dodecahedron, Fused Cubes, Face-Sharing and Edge-Sharing Pentagonal Prisms Hydrogen Bonding Networks." *Journal of Chemical Physics* 122(13):134304, 1-9.

Fu YJ, S Niu, T Ichiye, and LS Wang. 2005. "Electronic Structure and Intrinsic Redox Properties of $[2Fe\text{-}2S]^+$ Clusters with Tri- and Tetracoordinate Iron Sites." *Inorganic Chemistry* 44(5):1202-1204.

Fu YJ, X Yang, XB Wang, and LS Wang. 2004. "Terminal Ligand Influence on the Electronic Structure and Intrinsic Redox Properties of the $[Fe_4S_4]^{2+}$ Cubane Clusters." *Inorganic Chemistry* 43(12):3647-3655.

Fu YJ, X Yang, XB Wang, and LS Wang. 2005. "Probing the Electronic Structure of [2Fe-2S] Clusters with Three Coordinate Iron Sites by Use of Photoelectron Spectroscopy." *Journal of Physical Chemistry A* 109(9):1815-1820.

Gao F, EJ Bylaska, and WJ Weber. 2005. "Defect Properties in GaN: *ab initio* and Empirical Potential Calculations." *Materials Science Forum* 475-479:3087-3090.

Gaspar DJ, MH Engelhard, McHenry, and DR Baer. 2005. "Erosion Rate Variations during XPS Sputter Depth Profiling of Nanoporous Films." *Surface and Interface Analysis* 37(4):417-423.

Grate JW, NC Anheier, JR, and DL Baldwin. 2005. "Progressive Thermal Desorption of Vapor Mixtures from a Preconcentrator with a Porous Metal Foam Internal Architecture and Variable Thermal Ramp Rates." *Analytical Chemistry* 77(6):1867-1875.

Griffin KA, AB Pakhomov, CM Wang, SM Heald, and KM Krishnan. 2005. "Intrinsic Ferromagnetism in Insulating Cobalt Doped Anatase TiO_2." *Physical Review Letters* 94(15):157204, 1-4.

Harder E, B Kim, RA Friesner, and BJ Berne. 2005. "Efficient Simulation Method for Polarizable Protein Force Fields: Application to the Simulation of BPTI in Liquid Water." *Journal of Chemical Theory and Computation* 1(1):169-180.

Hornekaer L, A Baurichter, VV Petrunin, AC Luntz, BD Kay, and A Al-Halabi. 2005. "Influence of Surface Morphology on D_2 Desorption Kinetics from Amorphous Solid Water." *Journal of Chemical Physics* 122(12):124701, 1-11.

Hu JZ, JH Kwak, JE Herrera, Y Wang, and CHF Peden. 2005. “Line Narrowing in ^{1}H MAS Spectrum of Mesoporous Silica by Removing Adsorbed H_2O Using N_2.” *Solid State Nuclear Magnetic Resonance* 27(3):200-205.

Jaffe JE, TC Droubay, and SA Chambers. 2005. "Oxygen Vacancies and Ferromagnetism in $Co_xTi_{1-x}O_{2-x-y}$." *Journal of Applied Physics* 97(7):073908, 1-6.

Jiang W, V Shutthanandan, S Thevuthasan, CM Wang, and WJ Weber. 2005. "Nitrogen Analysis Using Energetic Ion Beams." *Surface and Interface Analysis* 37(4):374-378.

Kahn K and T Bruice. 2005. "Focal-Point Conformational Analysis of Ethanol, Propanol, and Isopropanol." *ChemPhysChem* 6(3):487-495.

Kaspar TC, T Droubay, CM Wang, SM Heald, AS Lea, and SA Chambers. 2005. "Co-Doped Anatase TiO_2 Heteroepitaxy on Si(001)." *Journal of Applied Physics* 97(7):073511, 1-10.

Laskin J and JH Futrell. 2005. “Activation of Large Ions in FT-ICR Mass Spectrometry.” *Mass Spectrometry Reviews* 24(2):135-167.

Lee CS, HJ Lee, SW Choi, J Kwak, and CHF Peden. 2005. "Structural and Catalytic Properties of the Alkali Metal Ion-Exchanged Y-Zeolites by ^{29}Si and ^{27}Al Solid-State NMR and FT-IR Spectroscopy." *Key Engineering Materials* 277-279:708-719.

Liang B, RD Hunt, GP Kushto, L Andrews, J Li, and BE Bursten. 2005. "Reactions of Laser-Ablated Uranium Atoms with H_2O in Excess Argon: A Matrix Infrared and Relativistic DFT Investigation of Uranium Oxyhydrides." *Inorganic Chemistry* 44(7):2159-2168.

Liu T, WJ Qian, WNU Chen, JM Jacobs, RJ Moore, DJ Anderson, MA Gritsenko, ME Monroe, BD Thrall, DG Camp II, and RD Smith. 2005. "Improved Proteome Coverage by Using High Efficiency Cysteinyl Peptide Enrichment: The Human Mammary Epithelial Cell Proteome." *Proteomics* 5(5):1263-1273.

Lu HP. 2005. “Site-Specific Raman Spectroscopy and Chemical Dynamics of Nanoscale Interstitial Systems.” *Journal of Physics: Condensed Matter* 17(7):R333-R355.

Lua YY, JJ Fillmore, L Yang, MV Lee, PB Savage, MC Asplund, and MR Linford. 2005. "First Reaction of a Bare Silicon Surface with Acid Chlorides and a One-Step Preparation of Acid Chloride Terminated Monolayers on Scribed Silicon." *Langmuir* 21(6):2093-2097.

Lynch DJ, WE Wilson, MT Batdorf, MB Sowa Resat, GA Kimmel, and JH Miller. 2005. “Monte Carlo Simulation of the Spatial Distribution of Energy Deposition for an Electron Microbeam.” *Radiation Research* 163(4):468-472.

Malloci G, G Mulas, G Cappellini, V Fiorentini, and I Porceddu. 2005. "Theoretical Electron Affinities of PAHs and Electronic Absorption Spectra of Their Mono-Anions." *Astronomy & Astrophysics* 432(2):585-594.

Markillie LM, CT Lin, JN Adkins, DL Auberry, EA Hill, BS Hooker, PA Moore, RJ Moore, L Shi, HS Wiley, and V Kery. 2005. "Simple Protein Complex Purification and Identification Method Suitable for High Throughput Mapping of Protein Interaction Networks." *Journal of Proteome Research* 4(2):268-274.

Nwe KH, SC Langford, JT Dickinson, and WP Hess. 2005. “Interaction of Wide-Band-Gap Single Crystals with 248-nm Excimer Laser Irradiation. X. Laser-Induced Near-Surface Absorption in Single-Crystal NaCl.” *Journal of Applied Physics* 97(4):043501, 1-5.

Nwe KH, SC Langford, JT Dickinson, and WP Hess. 2005. “Interaction of Wide-Band-Gap Single Crystals with 248-nm Excimer Laser Radiation. XI. The Effect of Water Vapor and Temperature on Laser Desorption of Neutral Atoms from Sodium Chloride.” *Journal of Applied Physics* 97(4):043502, 1-10.

Oostrom M, MD White, RJ Lenhard, PJ Van Geel, and TW Wietsma. 2005. “A Comparison of Models Describing Residual NAPL Formation in the Vadose Zone.” *Vadose Zone Journal* 4(1):163-174.

Page JS, B Bogdanov, AN Vilkov, DC Prior, MA Buschbach, K Tang, and RD Smith. 2005. “Automatic Gain Control in Mass Spectrometry using a Jet Disrupter Electrode in an Electrodynamic Ion Funnel.” *Journal of the American Society for Mass Spectrometry* 16(2):244-253.

Posselt M, F Gao, and D Zwicker. “Migration of Di- and Tri-Interstitials in Silicon.” *Nuclear Instruments and Methods in Physics Research Section B. Beam Interactions with Materials and Atoms* 228(1-4):212-217.

Rustad JR and AR Felmy. 2005. "The Influence of Edge Sites on the Development of Surface Charge on Goethite Nanoparticles: A Molecular Dynamics Investigation." *Geochimica et Cosmochimica Acta* 69(6):1405-1411.

Sasahara A, TC Droubay, SA Chambers, H Uetsuka, and H Onishi. 2005. "Topography of Anatase TiO_2 Film Synthesized on $LaAlO_3$ (001)." *Nanotechnology* 16(3):S18–S21.

Schultz NE and DG Truhlar. 2005. "New Effective Core Method (Effective Core Potential and Valence Basis Set) for Al Clusters and Nanoparticles and Heteronuclear Al-Containing Molecules." *Journal of Chemical Theory and Computation* 1(1):41-53.

Sendt K and BS Haynes. 2005. "Density Functional Study of the Reaction of Carbon Surface Oxides: The Behavior of Ketones." *Journal of Physical Chemistry A* 109(15):3438-3447.

Shin Y, LQ Wang, GE Fryxell, and GJ Exarhos. 2005. "Hygroscopic Growth of Self-Assembled Layered Surfactant Molecules at the Interface between Air and Organic Salts." *Journal of Colloid and Interface Science* 284(1):278-281.

Szanyi J, JH Kwak, J Hanson, C Wang, T Szailer, and CHF Peden. 2005. "Changing Morphology of BaO/Al_2O_3 during NO_2 Uptake and Release." *Journal of Physical Chemistry B* 109(15):7339-7344.

Turney JM, L Sari, Y Yamaguchi, and HF Schaefer, III. 2005. "The Singlet Electronic Ground State Isomers of Dialuminum Monoxide: AlOAl, AlAlO, and the Transition State Connecting Them." *Journal of Chemical Physics* 122(9):094304, 1-12.

Wang CM, S Azad, V Shutthanandan, DE McCready, CHF Peden, L Saraf, and S Thevuthasan. 2005. "Microstructure of ZrO_2-CeO_2 Hetero-Multi-Layer Films Grown on YSZ Substrate." *Acta Materialia* 53(7):1921-1929.

Wang CM, V Shutthanandan, S Thevuthasan, T Droubay, and SA Chambers. 2005. "Microstructure of Co-Doped TiO_2 (110) Rutile by Ion Implantation." *Journal of Applied Physics* 97(7):073502, 1-6.

Wang H, RC Bell, MJ Iedema, AA Tsekouras, and JP Cowin. 2005. "Sticky Ice Grains Aid Planet Formation: Unusual Properties of Cryogenic Water Ice." *Astrophysical Journal* 620(2):1027-1032.

Wu Q, AJ Cohen, and W Yang. 2005. "Excitation Energies from Time-Dependent Density Functional Theory with Accurate Exchange-Correlation Potentials." *Molecular Physics* 103(6-8):711-717.

Zhai HJ and LS Wang. 2005. "Chemisorption Sites of CO on Small Gold Clusters and Transitions from Chemisorption to Physisorption." *Journal of Chemical Physics* 122(5):051101, 1-4.

Presentations

The following list represents presentation by EMSL staff members and users where the presentations resulted from research carried out at EMSL.

Apra E. 2005. "Development of Quantum Chemistry Software on Parallel Computers." Presented by Edoardo Apra (Invited Speaker) at the Defense Advanced Research Projects Agency High-Performance Computing Petascale/s Compact Simulation Application Workshop, Argonne, Illinois, on March 21, 2005.

Ayotte P, JL Daschbach, Z Dohnalek, GA Kimmel, KP Stevenson, GR Teeter, RS Smith, and BD Kay. 2005. "Beakers Without Walls: Using Nanoscale Amorphous Films to Study Supercooled Water and Liquid Solutions." Presented by Bruce Kay (Invited Speaker) at the American Physical Society Meeting, Los Angeles, California, on March 21, 2005.

Ayotte P, JL Daschbach, Z Dohnalek, GA Kimmel, KP Stevenson, GR Teeter, RS Smith, and BD Kay. 2005. "Using Nanoscale Amorphous Films to Study Processes in Supercooled Liquid Water and Aqueous Solutions." Presented by Bruce Kay (Invited Speaker) at the University of Wisconsin, Madison, Wisconsin, on April 26, 2005.

Ayotte P, JL Daschbach, Z Dohnalek, GA Kimmel, RS Smith, KP Stevenson, and BD Kay. 2005. "Molecular Beam Studies of Dynamics and Kinetics on Ice and Oxide Surfaces." Presented by Bruce Kay (Invited Speaker) at the 229th American Chemical Society National Meeting, San Diego, California, on March 14, 2005.

Biju VP, M Micic, D Hu, and HP Lu. 2005. "Intermittent Single-Molecule Interfacial Electron Transfer Dynamics." Presented by H. Peter Lu (Invited Speaker) at the 229th American Chemical Society National Meeting, San Diego, California, on March 16, 2005.

Blake TA and PL Gassman. 2005. "Multivariate Curve Resolution Applied to Infrared Reflectance Measurements of Soil Contaminated with Organic Analyte." Presented by Paul Gassman (Invited Speaker) at the 12th International Conference on Near Infrared Spectroscopy, Sky City, Auckland, New Zealand, on April 11, 2005.

Camp DG, II, W Qian, T Liu, ME Monroe, N Jaitly, MA Gritsenko, RJ Moore, DJ Anderson, and RD Smith. 2005. "Quantitative Proteomic Profiling of Clinical Plasma Samples from Trauma Patients." Presented by David Camp (Invited Speaker) at the Glue Advisory Committee Meeting, Chicago, Illinois, on March 14, 2005.

Chambers SA. 2005. "Structure and Photochemistry at Oxide/Oxide Heterojunctions." Presented by Scott A. Chambers (Invited Speaker) at the 229th American Chemical Society National Meeting, San Diego, California, on March 15, 2005.

Cowin JP and MJ Iedema. 2005. "Proton Solvation and Motion in Water Ices and Their Interfaces." Presented by Jim Cowin (Invited Speaker) at the 229th American Chemical Society National Meeting, San Diego, California, on March 14, 2005.

de Jong WA, and HM Cho. 2005. "Rutherfordine and Pertechentate NMR: Interplay of Computational Modeling and Experiment." Presented by W. A. de Jong at the 45th Sanibel Symposium, St. Simons Island, Georgia, on March 8, 2005.

Devanathan R and WJ Weber. 2005. "Computational and Experimental Studies of the Radiation Response of $Gd_2Ti_2O_7$ Pyrochlore." Presented by Ram Devanathan (Invited Speaker) at the 107th Annual Meeting of the American Ceramic Society, Baltimore, Maryland, on April 11, 2005.

Devanathan R. 2005. "Computer Simulation of Defect Processes in Ceramics." Presented by Ram Devanathan (Invited Speaker) at the Department Seminar, Department of Materials Science and Engineering, University of Florida, Gainesville, Florida, on March 22, 2005.

Disselkamp RS, D Kim, J Kwak, CH Peden, J Szanyi, and RG Tonkyn. 2005. "Fundamental Studies of NOx Adsorber Materials." Presented by Chuck Peden (Invited Speaker) at the National Laboratory Advanced Combustion Engine R&D Merit Review and Peer Evaluation, Argonne, Illinois, on April 20, 2005.

Disselkamp RS, D Kim, J Kwak, CH Peden, J Szanyi, and RG Tonkyn. 2005. "Fundamental Studies of NOx Adsorber Materials." Presented by Chuck Peden (Invited Speaker) at the National Laboratory Advanced Combustion Engine R&D Merit Review and Peer Evaluation, Argonne, Illinois, on April 20, 2005.

Dixon DA, MS Gutowski, LA Pollack, TL Windus, and WA de Jong. 2005. "High Level Computational Approaches to the Prediction of the Thermodynamics of Chemical Hydrogen Storage Systems and Hydrocarbon Fuels." Presented by David A. Dixon (Invited

Speaker) at the 229th American Chemical Society National Meeting, San Diego, California, on March 15, 2005.

Dohnalek Z and BD Kay. 2005. "Growth and Catalytic Activity of Supported Nanoscaled Palladium Films." Presented by Zdenek Dohnalek (Invited Speaker) at the 229th American Chemical Society National Meeting, San Diego, California, on March 14, 2005.

Engelhard MH and DR Baer. 2005. "Challenges of Making Accurate and Useful XPS Measurements on Wide Variety of Materials in User Facility." Presented by Mark Engelhard (Invited Speaker) at the University of Central Florida, Orlando, Florida, on March 14, 2005.

Fanourgakis GS, A Lagutschenkov, K Kowalski, G Niedner-Schateburg, and SS Xantheas. 2005. "Structural, Spectral and Excited State Features of Water Hydrogen Bonding Networks: Results of ab-initio Calculations and Interaction Potentials." Presented by Sotiris S. Xantheas (Invited Speaker) at the 229th American Chemical Society National Meeting, San Diego, California, on March 13, 2005.

Felix EJ. 2005. "Active Storage and StorCloud." Presented by Evan Felix (Invited Speaker) Orientation to CRAY, Inc. Visitors, at Richland, Washington, on April 20, 2005.

Felix EJ. 2005. "Active Storage Processing in a Parallel File System." Presented by Evan Felix at the 6th LCI International Conference on Linux Clusters: The HPC Revolution 2005, Chapel Hill, North Carolina, on April 26, 2005.

Felix EJ. 2005. "Lustre at PNNL." Presented by Evan Felix (Invited Speaker) Orientation to CRAY Inc. Visitors, at Richland, Washington, on April 20, 2005.

Gallagher NB, TA Blake, and PL Gassman. 2005. "Application of Extended Inverse Scatter Correction to Mid-Infrared Reflectance Spectra of Soil." Presented by Neal Gallagher (Invited Speaker) at the 12th International Conference on Near Infrared Spectroscopy, Sky City, Auckland, New Zealand, on April 12, 2005.

Gallagher NB, TA Blake, and PL Gassman. 2005. "Multivariate Curve Resolution Applied to Infrared Reflectance Measurements of Soil Contaminated with Organic Analyte." Presented by Neal Gallagher (Invited Speaker) at the 12th International Conference on Near Infrared Spectroscopy, Sky City, Auckland, New Zealand, on April 11, 2005.

Gallagher NB, TA Blake, and PL Gassman. 2005. "Application of Extended Inverse Scatter Correction to Mid-Infrared Reflectance Spectra of Soil." Presented by Neal Gallagher (Invited Speaker) at the 12th International Conference on Near Infrared Spectroscopy, Sky City, Auckland, New Zealand, on April 12, 2005.

Grate JW, DA Nelson, RL Skaggs, MG Warner, and GC Dunham. 2005. "Advanced Materials for Chemical Sensors." Presented by Marvin Warner at the Homeland Security Research Conference: Working Together: Research & Development Partnerships in Homeland Security, Boston, Massachusetts, on April 27, 2005.

Grate JW. 2005. "Inorganic/Organic Materials for Chemical Vapor Sensors." Presented by Jay W. Grate (Invited Speaker) at the 229th American Chemical Society National Meeting, San Diego, California, on March 14, 2005.

Joly AG, WP Hess, G Xiong, DM Laman, JR Williams, and SA Chambers. 2005. "Carrier Lifetimes and Dynamics in Epitaxial Grown Fe_2O_3/Cr_2O_3 Thin Films Measured by Femosecond Transient Reflectivity and Absorption." Presented by Gang Xiong (Invited Speaker) at the American Physical Society Meeting, Los Angeles, California, on March 21, 2005.

Joly AG, WP Hess, G Xiong, DM Laman, JR Williams, and SA Chambers. 2005. "Carrier Lifetimes and Dynamics in Epitaxial Grown Fe_2O_3/Cr_2O_3 Thin Films Measured by Femosecond Transient Reflectivity and Absorption." Presented by Gang Xiong (Invited Speaker) at the American Physical Society Meeting, Los Angeles, California, on March 21, 2005.

Kayani AN, CV Ramana, RJ Smith, V Gorokhovsky, and V Shutthanandan. 2005. "High Temperature Oxidation Studies of Filtered Arc Deposited CrAlN Nanolayered Coatings on Steel Plates." Presented by R. J. Smith at the American Physical Society Meeting, Los Angeles, California, on March 5, 2005.

Kery V, JN Adkins, GA Anderson, DL Auberry, KJ Auberry, WR Cannon, DS Daly, YA Gorby, EA Hill, BS Hooker, JT Lin, EA Livesay, LM Markillie, PA Moore, RJ Moore, ES Peterson, RD Smith, HJ Sofia, KD Victry, and HS Wiley. 2005. "Automated Process for High-Throughput Mapping of Protein Interaction Networks." Presented by Vladimir Kery at the Keystone Symposia in Proteomics and Bioinformatics, Keystone, Colorado, on April 10, 2005.

Kimmel GA and NG Petrik. 2005. "Electron-Stimulated Reactions at the Interfaces of Thin Water Films on Pt(111)." Presented by Nik Petrik (Invited Speaker) at the 229th American Chemical Society National Meeting, San Diego, California, on March 13, 2005.

Komlos J, Jr., RK Kukkadapu, JM Zachara, and PR Jaffe. 2005. "Quantification of Iron Reoxidation in Microbially Reduced FRC Sediments." Presented by John Komlos at the 8th Annual Natural and Accelerated Bioremediation Research Principal Investigator Workshop, Warrenton, Virginia, on April 18, 2005.

Kowalski K. 2005. "Extensive Generalization of Renormalized Coupled-Cluster Methods." Presented by Karol Kowalski (Invited Speaker) at the 45th Sanibel Symposium, St. Simon's Island, Georgia, on March 9, 2005.

Kwak J, D Kim, J Szanyi, T Szailer, and CH Peden. 2005. "Reactivity of $Pt/BaO/Al_2O_3$ for NOx Storage/Reduction: Effects of Pt and Ba Loading." Presented by Chuck Peden at the 229th American Chemical Society National Meeting, San Diego, California, on March 15, 2005.

Laskin J. 2005. “Interaction of Peptide Ions with Self-Assembled Monolayer Surfaces.” Presented by Julia Laskin (Invited Speaker) at Hebrew University, Jerusalem, Israel, on April 4, 2005.

Li J. 2005. "Recent Developments of Computational Actinide Chemistry." Presented by Jun Li (Invited Speaker) at the 45th Sanibel Symposium, St. Simon's Island, Georgia, on March 7, 2005.

Liu J, H Fan, Q Huo, Y Wang, and CH Peden. 2005. "Designing Nanostructured Materials for Catalysis through Multiscale Growth and Self-Assembly." Presented by Jun Liu at the 229th American Chemical Society National Meeting, San Diego, California, on March 15, 2005.

Lu HP. 2005. “Single-Molecule Protein ‘Fly Fishing’ in Cell Signaling.” Presented by H. Peter Lu (Invited Speaker) at MMMS Annual Spring Meeting at Northwestern University, Evanston, Illinois, on March 24, 2005.

Lu HP. 2005. “Single-Molecule Spectroscopy Studies of Chemical Reaction Dynamics in Condensed Phase and at Interfaces.” Presented by H. Peter Lu at the Single Molecule Workshop, Rockville, Maryland, on April 10, 2005.

Minard KR, G Orr, M Zhang, JW Gunn, J Hu, and RA Wind. 2005. “Optical and Magnetic Resonance Imaging for Targeted Nanoparticle Development.” Presented by Kevin Minard at the NIBIB/DOE Workshop on Biomedical Applications of Nanotechnology, Bethesda, Maryland, on March 17, 2005.

Morgan WF and MB Sowa. 2005. “Using A Low LET Electron Microbeam to Investigate Non-Targeted Effects of Low Dose Radiation.” Presented by Marianne Sowa (Invited Speaker) at the DOE Low Dose Radiation Research Program Workshop, Bethesda, Maryland, on April 25, 2005.

Opresko L, MB Sowa, WB Chrisler, and MA Silva. 2005. “Mechanism(s) of Three-Dimensional Intercellular Signaling in Mammary Epithelial Cells in Response to Low Dose, Low-LET Radiation: Implications for the Radiation-Induced Bystander Effect.” Presented by Marianne Sowa (Invited Speaker) at the DOE Low Dose Radiation Research Program Workshop, Bethesda, Maryland, on April 25, 2005.

Orr G and A Gutowska. 2005. “Nanoscale Insight into Molecular Interactions in the Membrane of Living Cells; Implications in Nanoparticle-Protein Interactions and New Therapeutic Approaches.” Presented by Galya Orr (Invited Speaker) at the Oregon Health and Science University Workshop, Portland, Oregon, on March 17, 2005.

Ozensoy E, J Szanyi, and CH Peden. 2005. "Non-dissociative Adsorption of H_2O on Ordered Alumina Surfaces." Presented by Emrah Ozensoy at the 229th American Chemical Society National Meeting, San Diego, California, on March 15, 2005.

Pan D, D Hu, and HP Lu. 2005. “Site-Specific Resonance Raman Microscopy Studying Inhomogeneous Vibrational Relaxation Energy of Interfacial Electron Transfer.” Presented by Duohai Pan (Invited Speaker) at the 229th American Chemical Society National Meeting, San Diego, California, on March 15, 2005.

Petrik NG and GA Kimmel. 2005. "Low-Energy Electron-Stimulated Luminescence and Desorption from Thin Layers of Solid Water on Pt(111)." Presented by Nik Petrik (Invited Speaker) at the 229th American Chemical Society National Meeting, San Diego, California, on March 13, 2005.

Skouson GB. 2005. "Multicast Installation for Large Clusters." Presented by Gary Skouson at the 6th International Conference on Linux Clusters: The HPC Revolution 2005, Chapel Hill, North Carolina, on April 27, 2005.

Thevuthasan S, V Shutthanandan, SM Heald, TC Droubay, MH Engelhard, CM Wang, DE McCready, and SA Chambers. 2005. "Synthesis of Room-Temperature Ferromagnetic Oxide Materials by Ion Implantation." Presented by Theva Thevuthasan (Invited Speaker) at the American Vacuum Society Chapter Meeting in Florida, Orlando, Florida, on March 13, 2005.

Thevuthasan S. 2005. "Synthesis and Characterization of Oxide Nanostructures for Solid Oxide Fuel Cell Applications." Presented by Theva Thevuthasan (Invited Speaker) at the Seminar at University of Central Florida, Orlando, Florida, on March 17, 2005.

Valiev M. 2005. "Computational Studies of the Phosphorylation Reaction in Protein Kinase A: ab-initio QM/MM Approach." Presented by Marat Valiev at the 229th Americian Chemical Society National Meeting, San Diego, California, on March 17, 2005.

Wellman DM, SV Mattigod, BW Arey, PL Gassman, and SW Forrester. 2005. "In-Situ Identification of Solubility Limiting Uranium-bearing Minerals in Concrete." Presented by Dawn M. Wellman at the 229th American Chemical Society National Meeting, San Diego, California, on March 13, 2005.

Windus TL, Y Alexeev, E Apra, M Krishnan, V Tipparaju, BJ Palmer, and J Nieplocha. 2005. "Advanced Computational Methods Applied to Chemistry." Presented by Theresa Windus (Invited Speaker) at the 229th American Chemical Society National Meeting, San Diego, California, on March 14, 2005.