

EMSL Report

September/October 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 scientific consultant and users.

Research Highlights

Probing Inhomogeneous Vibrational Reorganization Energy Barriers of Interfacial Electron Transfer

D Pan,^(a) D Hu,^(a) and HP Lu^(a)

(a) Pacific Northwest National Laboratory, Richland, Washington

Understanding the dynamics of electron transfer may lead to improved nanoparticle catalysts for energy and environmental applications.

Interfacial electron-transfer processes in dye-sensitized semiconductor systems often involve complex and inhomogeneous dynamics. The complexity and inhomogeneity come from the spatial heterogeneities of the surfaces and the inhomogeneous vibronic coupling between the adsorbed molecules and the nanoscale rough surfaces of the substrates. Recently, there has been much interest in the use of TiO₂ particles as photo-oxidation catalysts. To better utilize these particles, a fundamental understanding of the electron-transfer process is needed. However, our current knowledge of the spatial and temporal inhomogeneities of interfacial electron-transfer dynamics is inadequate to characterize the heterogeneous local environments of

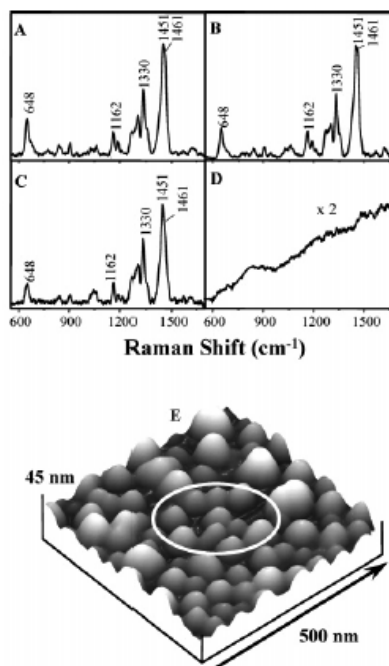


Figure 1. Resonance Raman and AFM characterization of alizarin/TiO₂ interfacial electron transfer.

nanoparticles and the nanoscale roughness on the surfaces of the substrates. Interfacial electron-transfer dynamics can be different from site to site and from time to time and can involve both static and dynamic inhomogeneities. Presumably, the inhomogeneity and fluctuations of the local driving force, the vibrational reorganization energy, the solvent reorganization energy, the electronic and Franck-Condon couplings, and the electron trapping and scattering at the interfaces and in the bulk of the semiconductor substrates could all contribute to the complexity and inhomogeneity in interfacial electron-transfer dynamics.

In this study, we used both resonance Raman microscopy and atomic force microscopy (AFM) to characterize the vibrational reorganization energy barriers of the interfacial electron transfer in a dye-sensitization system, namely, alizarin adsorbed on TiO_2 nanoparticles. Figure 1 shows a representative experiment where we simultaneously obtained a resonance Raman spectrum and AFM image. We observed that the Raman peak intensity and peak-to-peak intensity ratio are different among different submicrometer-scale spots at the TiO_2 nanoparticle layer. We then focused on revealing inhomogeneous vibrational reorganization energy barriers for interfacial electron transfer, using a time-dependent wave packet propagation analysis of resonance Raman spectra to obtain mode-specific vibrational reorganization energies upon the charge-transfer reactions for individual spots under a 250-nm spatial resolution. Although the spatial resolution of our Raman spectroscopy was not at nanoscale, our results present a significant step forward in characterizing site-specific vibrational reorganization energy and shed light on inhomogeneous interfacial electron-transfer dynamics in terms of inhomogeneous Franck-Condon barriers.

Applying microscopic AFM-Raman characterization and analysis, we revealed that, for alizarin/ TiO_2 interfaces, the vibrational reorganization energy barriers of interfacial electron transfer are inhomogeneous at a sub-mesoscale (250 nm). We found that (1) the total vibrational reorganization energy was inhomogeneous from site to site; (2) the alizarin/ TiO_2 bridging normal modes were the primary contributor to the total vibrational reorganization energy and its inhomogeneity; (3) the mode-specific analyses indicated that the energy distributions were inhomogeneous for bridging normal modes and less inhomogeneous or homogeneous for non-bridging normal modes, especially for modes far away from the alizarin- TiO_2 coupling hydroxyl modes; and (4) the vibrational reorganization energy inhomogeneity was closely associated with the local environmental heterogeneity of the alizarin/ TiO_2 interface. It is most likely that the vibrational

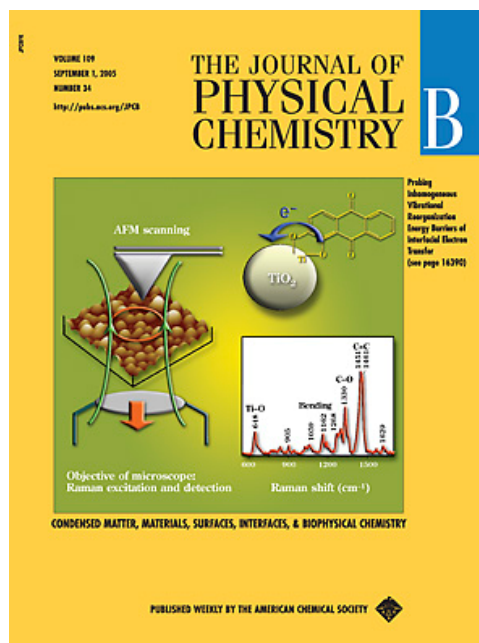


Figure 2. Cover of the September 1, 2005, issue of *Journal of Physical Chemistry B*.

reorganization energy inhomogeneities contributed to the inhomogeneous dynamics of the interfacial electron-transfer processes. However, it is still a challenge to identify a detailed mechanism of the contribution of the inhomogeneity to both forward and backward electron-transfer processes in the alizarin/TiO₂ system. Although the topographic and spectroscopic detection limits reported here have not yet reached single molecules, single semiconductor nanoparticles, or even nanoscale-specific sites, our results demonstrated that correlated AFM-confocal Raman microscopy is a promising approach for a quantitative understanding of inhomogeneous interfacial charge transfers.

This exciting research was featured on the September 1, 2005, cover of the *Journal of Physical Chemistry B* (Figure 2).

Citation

Pan D, D Hu, and HP Lu. 2005. "Probing Inhomogeneous Vibrational Reorganization Energy Barriers of Interfacial Electron Transfer." *Journal of Physical Chemistry B* 109(34):16390-16395.

Unusual Aggregates from the Oxidation of Alkene Self-Assembled Monolayers: A Previously Unrecognized Mechanism for SAM Ozonolysis?

TM McIntire,^(a) AS Lea,^(b) DJ Gaspar,^(b) N Jaitly,^(b) Y Dubowski,^(c) Q Li,^(a) and BJ Finlayson-Pitts^(a)

(a) University of California, Irvine, California

(b) W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington

(c) Technion-Israel Institute of Technology, Haifa, Israel

In conjunction with literature reports of polymer formation from VOC-NO_x photooxidations, formation of aggregates and polymers in the atmosphere may be much more widespread than previously thought.

Airborne particles have well-documented effects on human health, visibility, and the chemistry and radioactive properties of the atmosphere. Mineral dust, of which silica is commonly a major component, adsorbs organic compounds that are oxidized during transport. Oxidation is thought to convert hydrophobic coatings into polar, hydrophilic coatings that will adsorb increased amounts of water, influencing the chemical and radiative properties of the particles. However, present studies show that as oxidation proceeds, the underlying substrate is increasingly exposed. This suggests that the model of conversion of fully coated organic hydrophobic particles into a uniform, hydrophilic coating that takes up increased amounts of water may not, indeed, be the case.

In the present study, self-assembled monolayers (SAMs) of vinyl-terminated 3- and 8-carbon compounds were generated on silica substrates and reacted at room temperature with ~ 1 ppm gaseous ozone (O_3). A combination of atomic force microscopy (AFM), scanning electron microscopy, Auger electron spectroscopy, and time-of-flight secondary ion mass spectrometry was used to study the surface composition and morphology after oxidation.

AFM imaging of the organic-coated sample showed a relatively smooth surface as expected for a SAM on silicon (Figure 3). However, after oxidation with O_3 , large, irregular particles with dimensions varying from tens of nanometers to several microns were observed. Furthermore, the substrate surrounding these irregular particles became depleted of carbon compared to the unreacted SAM. Long-chain C8- and C12-saturated SAMs generated on a silicon substrate and exposed to O_3 under similar conditions, however, showed no evidence of agglomeration. This highly unusual result establishes that the mechanism of ozonolysis of alkene SAMs must have a channel that is unique compared to that in the gas phase or in solution, and may involve polymerization induced by the Criegee intermediate (CI). Oxidation at 60% relative humidities (RH) led to the formation of a number of smaller aggregates (as shown in Figure 3d), suggesting water intercepted the CI in competition with aggregate formation.

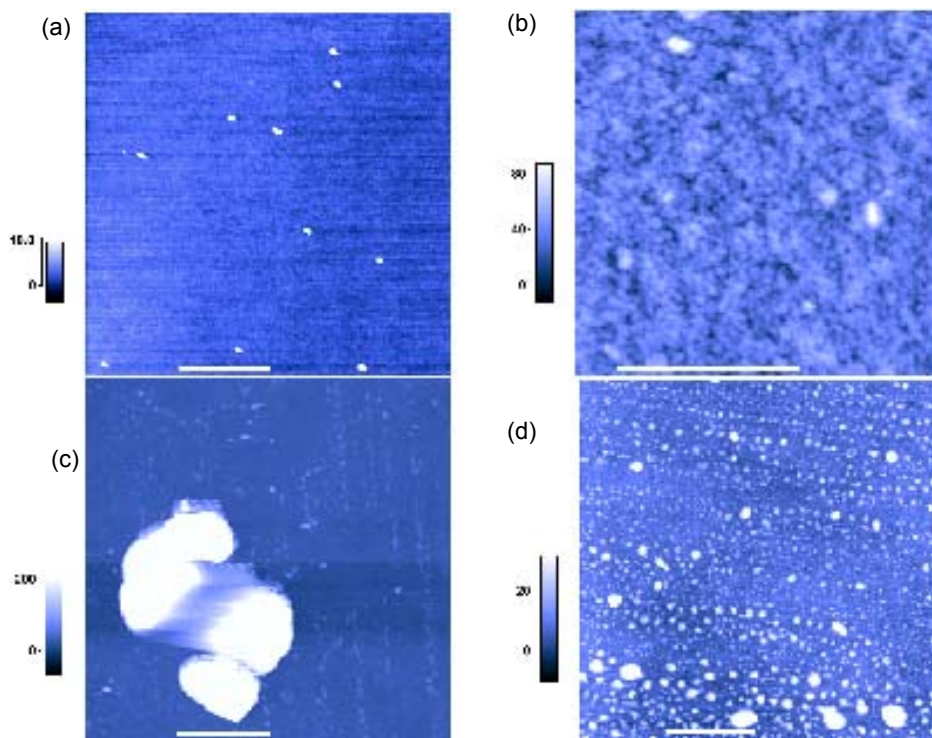


Figure 3. Intermittent contact mode AFM images of (a) a clean silicon substrate; (b) a silicon substrate on which a C8= SAM has been deposited; (c) as in (b) but after reaction with $\sim 10^{13}$ molecules cm^{-3} O_3 for 40 minutes; and (d) a C8= SAM after ozone oxidation in presence of water at 60% RH. The scale bar in all images is 500 nanometers.

This suggests that the model of conversion of fully coated organic hydrophobic particles into a uniform, hydrophilic coating that takes up increased amounts of water may not, indeed, be the case. In fact, we have found that uptake of water, measured using transmission Fourier transform infrared spectrometry, was not increased upon oxidation of these films. Figure 4 shows the amount of surface-adsorbed water at equilibrium at various RH for an unreacted C8= SAM, an ozone-oxidized C8= SAM and, for comparison, an unreacted saturated C18 SAM, all on quartz substrates. The water adsorbed on the less-ordered, unreacted C8= SAM is larger than on the well-ordered, relatively defect-free C18 SAM. This is consistent with defects and imperfections on the C8= SAM through which water can penetrate to the substrate. However, there is no difference in water uptake before and after the oxidation of the C8= SAM. The C3= SAM showed similar behavior. For SAM monolayers and lower concentrations of ozone, oxidation of the SAM clearly does not lead to enhanced water uptake, which may be due to control of water uptake by the substrate for both the reactant and for the oxidized sample.

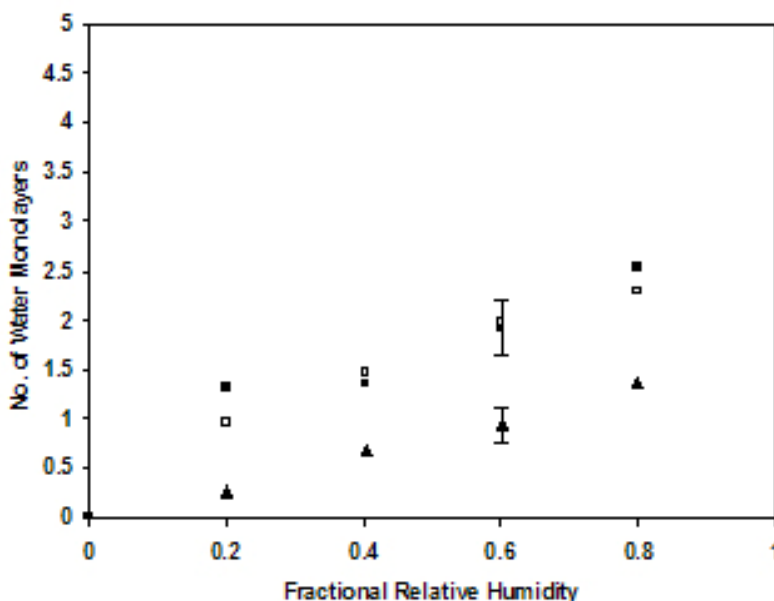


Figure 4. Water uptake as a function of RH at 295 K measured using Fourier transform infrared spectrometry. C18 SAM (▲); C8= SAM (■); and C8= after reaction with $\sim 10^{13}$ molecules cm^{-3} O₃ for 40 min (□). Representative error bars are given for the C18 and oxidized C8= SAMs.

Ozone, a toxic air pollutant for which air quality standards are set, is found in the atmosphere globally at ~ 30 to 40 ppb in remote regions, and at higher levels in polluted areas. The results presented here suggest that alkene SAMs may not have long-term stability in ambient air that contains even “background” amounts of ozone and that the formation of these large organic aggregates may occur more generally when alkenes are present on a

surface. In addition, this oxidation leads to surface segregation of the organic material, which will change the interactions of the particle with biological systems in ways that remain to be explored. In studies of the atmospheric oxidation of organic compounds, less than 50% of the condensed-phase products in particles have typically been identified. Recent laboratory studies indicate that the missing material is at least in part polymeric. Whether the reactions leading to the polymers require acid catalysis is not clear. However, the present studies show that the formation of organic aggregates and/or polymeric material in airborne particles may be a quite general phenomenon that is not restricted to reactions of secondary organics in the liquid phase, nor to acid-catalyzed chemistry.

Further details on this research can be found in McIntire et al. 2005.

Citation

McIntire TM, AS Lea, DJ Gaspar, N Jaitly, Y Dubowski, Q Li, and BJ Finlayson-Pitts. 2005. "Unusual Aggregates from the Oxidation of Alkene Self-Assembled Monolayers: A Previously Unrecognized Mechanism for SAM Ozonolysis?" *Physical Chemistry Chemical Physics: PCCP* 7(20):3605-3609.

Surface Studies on Highly Active CeO₂-Supported Cu-Pd Bimetallic Catalysts for the Oxygen-Assisted Water-Gas-Shift Reaction

EB Fox,^(a) MH Engelhard,^(b) S Velu,^(a) and C Song^(a)

(a) Pennsylvania State University, University Park, Pennsylvania

(b) W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington

Better catalytic performance has been observed using Cu-Pd bimetallic catalysts over monometallic catalysts containing copper alone or palladium alone supported on the CeO₂ support. However, the role of copper and palladium in the catalytic performance and the surface nature of the Cu-Pd bimetallic catalysts have not been well understood. The objective of the present work is to investigate the role of palladium on the catalytic performance in the oxygen-assisted water-gas-shift reaction to achieve carbon monoxide reduction. Such catalysts have potential use in proton exchange membrane fuel cells.

Reformed hydrocarbon fuels may become an important source of hydrogen for proton exchange membrane fuel cells. In order to use these hydrogen sources, however, low levels of sulfur and carbon monoxide must be achieved. In a conventional fuel reformer for fuel cell feed gases, the carbon monoxide reduction steps of the high- and low-temperature water-gas-shift and referential oxidation can take up more than 50% of the fuel cell systems volume and weight. In order to reduce volume, the water-gas-shift and PdOx reactions are combined and performed in a single step called oxygen-assisted water-gas-shift (OWGS) reaction (Bickford et al. 2005). We recently developed a new series of highly active and less pyrophoric Cu-Pd bimetallic catalysts supported on high-surface-area CeO₂ catalysts for the

OWGS. A catalyst containing about 30 wt % copper and 1 wt % palladium has been found to be optimum in order to achieve high carbon monoxide conversion, close to 100% around 230°C. The effect of temperature and space velocity on catalytic performance has been evaluated. In the present study, we employed *in-situ* x-ray photoelectron spectroscopy (XPS) and *in-situ* Fourier transform infrared spectroscopy studies on the Cu-Pd/CeO₂ catalysts in order to understand the nature of active species involved in the OWGS reaction.

The synthesis and characterization of various high-surface-area CeO₂ supports and Cu-Pd/CeO₂ catalysts have been described in our recent publication. Copper and palladium were impregnated over a CeO₂ support in two steps, first copper followed by palladium. XPS measurements of both unreduced as well as reduced catalysts were performed by a “pseudo *in-situ* method” at EMSL. About 100 mg of the catalysts were loaded in a quartz reactor and reduced under 5% H₂/Ar mixture (50 cc/min). The samples were reduced at a heating rate of 5°C/min up to 225°C and maintained at this temperature for about 1 hour before cooling to room temperature. The reactor was sealed and transferred into a glove box with O₂ concentration maintained below 0.4 ppm. In the glove box, the reduced catalysts were retrieved and mounted for XPS analysis. The samples were then loaded into the XPS chamber without exposure to air (Henderson et al. 2003).

XPS data of three samples, namely Cu(30)Pd(0)/CeO₂ containing only copper without palladium, Cu(0)Pd(1)/CeO₂ containing only palladium without copper, and Cu(30)Pd(1)/CeO₂ containing both copper and palladium in the unreduced as well as reduced form have been collected in order to understand the effect of palladium on the surface chemical properties of Cu/CeO₂ catalysts. The unreduced samples exhibited peaks corresponding to Cu²⁺, Pd²⁺, and Ce⁴⁺ species in these samples. Upon reduction around 225°C, the Cu²⁺ and Pd²⁺ species are reduced mainly to their metallic states, while cerium exists mainly in the Ce⁴⁺ state.

Figure 5 shows the XPS spectra of reduced Cu-Pd/CeO₂ catalysts in the copper 2p and palladium 3d regions. The copper 2p XPS spectra exhibit sharp peaks around 932 eV for metallic copper species. Significant differences in peak position and spectral intensity could be noticed in the copper 2p spectra. Addition of palladium to the copper/CeO₂ catalyst shifts the copper 2p_{3/2} peak position towards lower binding energy by about 0.4 eV [932.4 eV for Cu(30)Pd(0)/CeO₂ and 932.0 eV for Cu(30)Pd(1)/CeO₂ catalysts], indicating that the reducibility of copper is improved by the addition of palladium. This also leads to a decrease in intensity of the copper 2p peak, suggesting that the surface dispersion of copper is improved by the addition of palladium. The XPS spectra collected in the valence band region, below 10 eV, showed that copper 3d bands are located close to the Fermi energy (EF=0), indicating that copper is mainly involved in chemical interaction, converting carbon monoxide into CO₂. The overall spectral intensity decreased upon addition of palladium, further supporting the core level observation that copper dispersion is improved by the addition of palladium. The XPS spectra in the palladium 3d region indicate that the palladium is present mostly in Pd⁰ state in the catalyst containing both copper and palladium, while a significant amount of Pd⁺ and/or Pd²⁺ is present in the catalyst without copper. The presence of copper helps to retain palladium in its metallic state. Thus, the existence of a synergistic interaction between copper and palladium in the Cu-Pd bimetallic catalysts supported on CeO₂ is clearly seen from the XPS data. The existence of Cu-Pd alloy

on the surface of these Cu-Pd bimetallic catalysts could be responsible for the higher catalytic activity for carbon monoxide oxidation (Hungria et al. 2002).

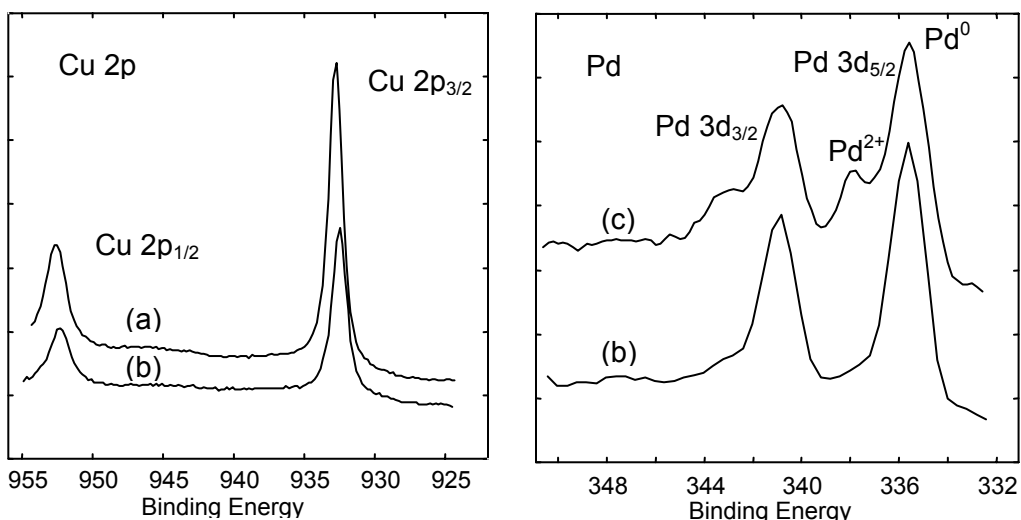


Figure 5. Copper 2p and palladium 3d XPS spectra of Cu-Pd/CeO₂ catalysts; (a) Cu(30)Pd(0)/CeO₂; (b) Cu(30)Pd(1)/CeO₂; and (c) Cu(0)Pd(1)/CeO₂.

Citations

Bickford ES, S Velu, and C Song. 2005. "Nano-Structured CeO₂ Supported Cu-Pd Bimetallic Catalysts for the Oxygen-Assisted Water-Gas-Shift Reaction." *Catalysis Today* 99(3-4):347-357.

Henderson MA, CL Perkins, MH Engelhard, S Thevuthasan, and CHF Peden. 2003. "Redox Properties of Water on the Oxidized and Reduced Surfaces of CeO₂(111)" *Surface Science* 526(1-2):1-18.

Hungria AB, A Iglesias-Juez, A Martinez-Arias, M Fernandez-Garcia, JA Anderson, JC Conesa, and J Soria. 2002. "Effects of Copper on the Catalytic Properties of Bimetallic Pd-Cu/(Ce,Zr)O_x/Al₂O₃ and Pd-Cu/(Ce,Zr)O_x Catalysts for CO and NO Elimination." *Journal of Catalysis* 206(2):281-294.

Luminescence from the trans-Dioxotechnetium(V) Chromophore

A Del Negro,^(a) Z Wang,^(a) CJ Seliskar^(b), WR Heineman^(b), BP Sullivan,^(c) SE Hightower^(c), TL Hubler,^(a) and SA Bryan^(a)

(a) Pacific Northwest National Laboratory, Richland Washington

(b) University of Cincinnati, Cincinnati, Ohio

(c) University of Wyoming, Laramie, Wyoming

Subsurface contamination by technetium is of particular concern because of the extremely long life of its most common isotope, ⁹⁹Tc, and the fast migration in soils exhibited by its most common chemical form, pertechnetate. This research contributes to the potential to develop an electrochemical-fluorescence-based sensor to detect technetium in contaminated groundwater at the Hanford Site and elsewhere.

Funded by DOE's Environmental Management Science Program, this research features a collaboration among researchers from the University of Cincinnati (CJ Seliskar and WR Heineman), University of Wyoming (BP Sullivan and SE Hightower), and PNNL (TL Hubler, SA Bryan, A Del Negro, and Z Wang). The work involves the spectroelectrochemical detection of pertechnetate in the vadose zone. Subsurface contamination by technetium is of particular concern because of the extremely long life of its most common isotope, ⁹⁹Tc (half-life = 2×10^5 years), and the fast migration in soils exhibited by its most common chemical form, pertechnetate (TcO_4^-). A sensor is being designed that has the capability for onsite monitoring, either by immersion in subsurface water for continuous monitoring or for immediate analysis of collected samples. The device combines electrochemistry, spectroscopy, and selective partitioning capabilities, the combination of which substantially improves selectivity.

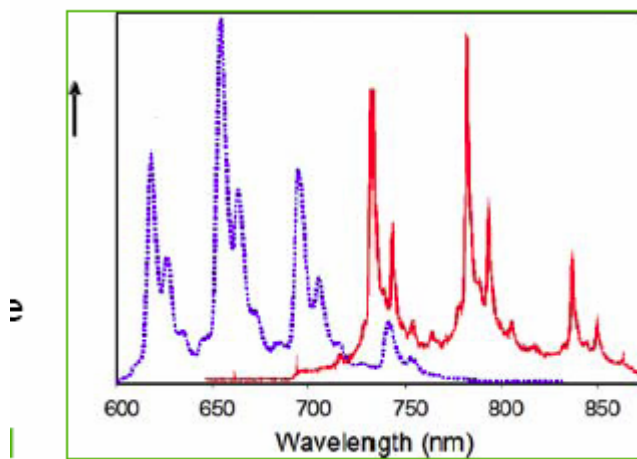


Figure 6. Low-temperature (8 K) luminescence spectra of microcrystalline $[\text{ReO}_2(\text{pic})_4](\text{BPh}_4)$ (blue) and $[\text{TcO}_2(\text{pic})_4](\text{BPh}_4)$ (red). Spectra are not normalized for excitation intensity differences.

A Del Negro and Z Wang measured the luminescence and excited-state lifetime properties of a newly discovered Tc(V) chromophore using EMSL's Liquid Helium Line Narrowing Laser-Induced Time-Resolved Fluorescence System. Their research has led to the discovery of the first luminescence from trans-dioxo-technetium(V) complexes. The room- and low-temperature luminescence studies of trans-[TcO₂(L)₄]⁺ (L = pyridine or picoline) and trans-[TcO₂(CN)₄]³⁻ opens a new chapter in technetium chemistry, both in a fundamental and practical sense. The low-temperature luminescence spectrum (Figure 6) for [TcO₂(pic)₄](BPh₄), with [ReO₂(pic)₄](BPh₄) shown as an overlay spectrum, clearly shows a lower-energy (~180-200 cm⁻¹) vibronic progression for analogous rhenium and technetium complexes. This important development allows the researchers to develop a theoretical model that can be used to predict the optical behavior of technetium complexes in general.

This discovery also provides the first opportunity to directly compare fundamental luminescence properties of second- and third-row d2 metal-oxo congeners. The analytical applications of the TcO₂ chromophore offer promise for design of dual-mode complexes that can correlate luminescence and radioimaging properties into a single agent. For the project's purposes, luminescent Tc(V) complexes are a significant advance in the team's design of a spectroelectrochemical sensor for detection of pertechnetate in the environment.

Measurements to determine quantum yield and absorption spectral data as well as detailed studies of the temperature dependence of the photophysical properties of the technetium complexes are currently underway.

Mistranslation Fragment of an *in silico* Designed Novel-Fold Protein Forms an Exceptionally Stable Symmetric Homodimer with a High-Affinity Interface

G Dantas,^(a) AL Watters,^(a) BM Lunde,^(a) ZM Eletr,^(b) NG Isern,^(c) J Lipfert,^(d) S Doniach,^(d) BA Kuhlman,^(b) BL Stoddard,^(e) G Varani,^(a) and D Baker^(a)

(a) University of Washington, Seattle, Washington

(b) University of North Carolina, Chapel Hill, North Carolina

(c) William R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington

(d) Stanford University, Stanford, California

(e) Fred Hutchinson Cancer Research Center, Seattle, Washington

The last decade has seen tremendous advances in the field of computational protein design. Designed proteins with high thermodynamic stabilities may allow generation of longer-lasting species useful in industrial applications and therapeutics.

In silico protein sequence and structure optimization algorithms have been successfully applied to redesign proteins and to create novel protein structures. Designed proteins may

achieve thermodynamic stabilities greater than those reported for any naturally occurring proteins. An obvious application of these exceptionally stable proteins is the generation of longer-lasting designer proteins for therapeutics. However, while exceptional protein stability offers advantages in resistance to proteolysis and unfolding, there may also be biological costs once these proteins are expressed or delivered in the cell. Since exceptionally stable computationally designed proteins are created in the absence of specific evolutionary pressure, they provide a rare opportunity to reveal aspects of the cellular protein production and surveillance machinery that are subject to natural selection.

Using purely computational techniques, researchers at the University of Washington recently generated an extremely stable, small, globular protein, called Top7, with a sequence and fold not observed previously in nature. In collaboration with scientists at Stanford University, the University of North Carolina Chapel Hill, Fred Hutchinson Cancer Research Center, and Pacific Northwest National Laboratory's High-Field Magnetic Resonance Facility, the University of Washington researchers have now demonstrated that a region of the Top7 protein corresponding to the final 49 C-terminal residues is efficiently mistranslated in *E. coli*, and that the solution structure of the resulting CFr protein is a compact, stable obligate homodimer (Figure 7). EMSL's 600-MHz cryoprobe was instrumental in collecting data that allowed CFr dimer structure determination, including collection of C^{12}/C^{13} edited/filtered experiments. The solution nuclear magnetic resonance (NMR) structure reveals that the CFr dimer has a novel symmetric interface formed by two identical CFr subunits, and analysis of NMR backbone dynamics further confirmed the rigidity of the structure. In addition, the researchers have determined that stabilization of CFr by disulfide-induced covalent circularisation yields a super-stable miniature protein that can serve as a robust scaffold for further protein engineering. Current efforts using CFr and SS.CFr as scaffolds include preparation of epitope-peptides for production of antibodies against human immunodeficiency virus and functionalization with peroxide-activating catalysts for bioremediation.

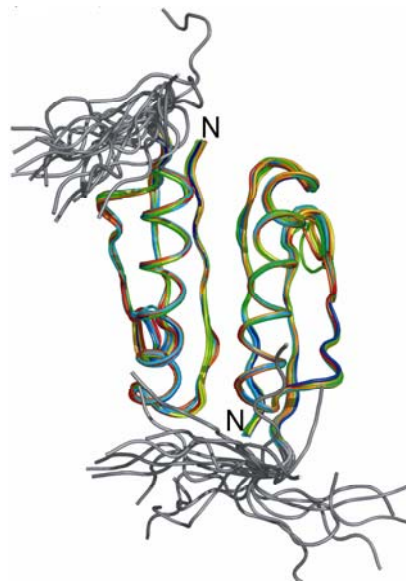


Figure 7. NMR-generated structures of CFr. The top 20 NMR models from the final CFr structure calculation are shown as ribbons. Each model is superimposed on the average backbone coordinates for residues 3–51 (structured region, separate color for each model) in both chains from the entire ensemble. The structured regions have an ensemble RMSD of 0.33Å over the backbone atoms and 0.75Å over all heavy-atoms. Residues from the unstructured tails (52–58) are colored in grey.

Proteome of the *Yersinia pestis* Type III Secretion System: Insights into the Injectisome

KK Hixson,^(a) SL McCutchen–Maloney,^(b) RD Smith,^(c) and MS Lipton^(c)

(a) W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington

(b) Lawrence Livermore National Laboratory, Livermore, California

(c) Pacific Northwest National Laboratory, Richland, Washington

*We are becoming ever more concerned with the reemergence of pandemic diseases, such as that expected with the so-called “bird flu.” Our most effective means of protecting ourselves will be to gain better understanding of how infecting organisms cause diseases. *Y. pestis* is the causative agent of the “Black Death” or bubonic plague, and our work with this bacterium is an important step to understanding which proteins are used by the microbe to infect other cells.*

The type III secretion system (TTSS) is an essential virulence mechanism of pathogenic *Yersinia* spp (Cornelis 2002a; Mota and Cornelis 2005). The TTSS is composed of a syringe-like secretion structure (injectisome) that is made up of a basal protein complex that provides a portal through the inner membrane and periplasmic space (Cornelis 2002b), an outer membrane channel protein (YscC) (Burghout et al. 2004), and the needle which grows to pierce the host cell membrane through successive polymerization of the protein YscF (Hoiczyk and Blobel 2001). Once constructed, the TTSS participates as a channel to direct effector proteins, known as Yops, into the host cell cytoplasm (Viboud and Bliska 2005). The Yops then act on the host cell to promote pathogenesis by disrupting the cytoskeleton, preventing phagocytosis, and blocking the production of proinflammatory cytokines (Cornelis 2002a). This assault on the host allows *Yersinia pestis* to easily propagate with minimal detection or interference (Cornelis et al. 2002a).

Yersinia pestis was grown in four conditions that mimicked growth either in the flea vector (26°C with or without calcium) or mammalian host (non-contact state: 37°C with calcium and a host cell contact state, 37°C without calcium) (Fowler and Brubaker 1994). Current hypotheses theorize that the injectisome is already preformed before host cell contact at the onset of the temperature increase (Cornelis 2002a; Edqvist et al. 2003). We however, only identified components of the injectisome under conditions that mimic host cell attachment (37°C without calcium).

Figure 8 shows the injectisome components identified using the accurate mass and time (AMT) tag approach to proteomics. Figures 8A through D show the theoretical assembled components of the injectisome in conditions that mimic growth in the flea or mammalian host. The indication of these results is that the injectisome assembly does not occur in any appreciable amount until the bacteria attach themselves directly to the mammalian cell. Attachment then triggers the formation of the injectisome and allows for translocation of the Yop proteins responsible for host cell destruction and host immune system diversion.

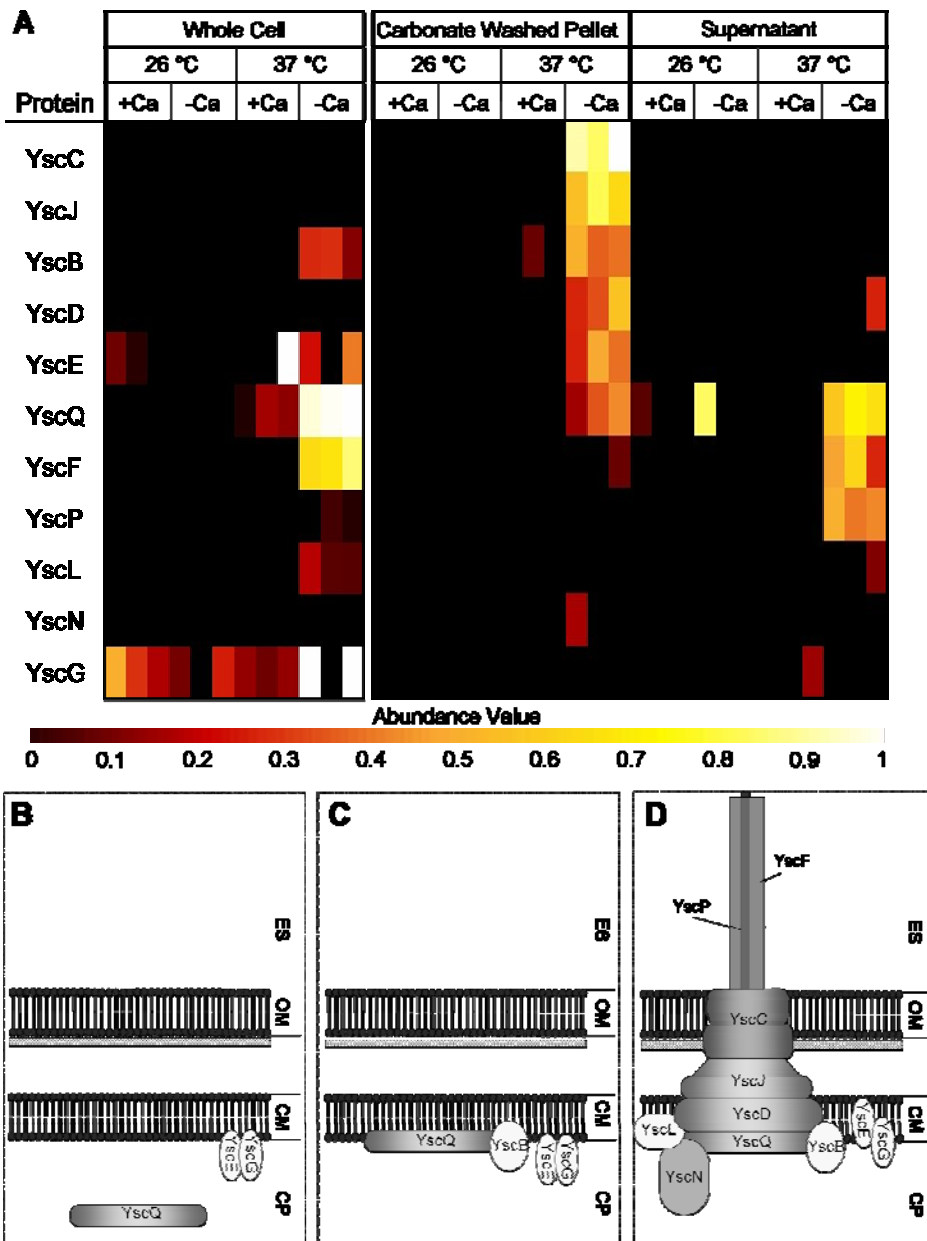


Figure 8. Abundance value comparisons of 11 injectisome components measured by the AMT tag proteomics methods for four growth conditions representing *Y. pestis* growth in a flea or mammalian host. (A) Heat-map representation of the abundance value. (B) Schematics of the theoretical assembled component of the injectisome at (B) 26 °C, (C) 37 °C with Ca²⁺, and (D) 37 °C without Ca²⁺. ES, extracellular; OM, outer membrane; CM, cytoplasmic membrane; CP, cytoplasm.

Citations

- Burghout P, R van Boxtel, P Van Gelder, P Ringler, SA Muller, J Tommassen, and M Koster. 2004. "Structure and Electrophysiological Properties of the YscC Secretin from the Type III Secretion System of *Yersenia enterocolitica*." *Journal of Bacteriology* 186(14):4645-4654.
- Cornelis GR. 2002a. "Yersenia Type III Secretion: Send in the Effectors." *Journal of Cell Biology* 158(3):401-408.
- Cornelis GR. 2002b. "The Yersenia Ysc-Yop Virulence Apparatus." *International Journal of Medical Microbiology* 291(6-7):455-462.
- Edqvist PJ, J Olsson, M Lavander, L Sundberg, A Forsberg, H Wolf-Watz, and SA Lloyd. 2003. "YscP and YscU Regulate Substrate Specificity of Yersenia Type III Secretion System." *Journal of Bacteriology* (185(7):2259-2266.
- Fowler JM, and RR Brubaker. 1994. "Physiological Basis of the Low Calcium Response in *Yersenia pestis*." *Infection and Immunity* 62(12):5234-5241.
- Hoiczky E, and G Blobel. 2001. "Polymerization of a Single Protein of the Pathogen *Yersenia enterocolitica* into Needles Punctures Eukaryotic Cells." *Proceedings of the National Academy of Sciences of the United States of America* 98(8):4669-4674.
- Mota LJ, and GR Cornelis. 2005. "The Bacterial Injection Kit: Type III Secretion Systems." *Annals of Medicine* 37:234-249.
- Viboud GI, and JB Bliska. 2005. "Yersenia Outer Proteins: Role in Modulation of Host Cell Signalling Responses and Pathogenesis." *Annual Review of Microbiology* 59.

Are Solvation Free Energies of Homogeneous Helical Peptides Additive?

R Staritzbichler,^(a) W Gu,^(a) and V Helms^(b)

(a) Saarland University, Saarbrücken, Germany

(b) Max Planck Institute for Biophysics, Frankfurt, Germany

Validation of simple, efficient models to describe protein-water interactions are critical to large scale biological simulations.

Solvation effects are an important component of many biochemical processes where solute (e.g. peptide chains) are being transferred from an aqueous environment to a less polar medium. The accurate description of solvation effects is therefore an essential part of any systematic approach aiming at contributing to the understanding of such processes.

Methods based on the explicit treatment of solvent using multiconfiguration thermodynamic integration (MCTI) or free-energy perturbation approaches provide an accurate and reliable way to calculate solvation effects. This accuracy, however, comes at considerable computational cost, rendering these methods expensive for large systems. Implicit solvent methods represent another way to calculate solvation effects. In these methods, solvent degrees of freedom are not represented explicitly but rather treated as a mean field property. This treatment assumes that solvation-free energy contributions from neighboring segments are to some extent additive. The validity of this assumption is investigated in this work by performing both explicit MCTI and implicit generalized-born surface area (GBSA) model calculations. All MCTI calculations (Figure 9) were performed using the NWChem computational chemistry package. The results of this work indicate that MCTI and GBSA give similar results in the case of five more residues. Sizable differences are found for short peptide chains. Both methods show nonadditivity of solvation-free energies for short (less than 5) peptide chains. Other GBSA calculations indicate that additivity is fulfilled for helices longer than 10 residues. These results suggest caution must be exercised when extrapolating implicit solvation parameters from small to large molecules and vice versa.

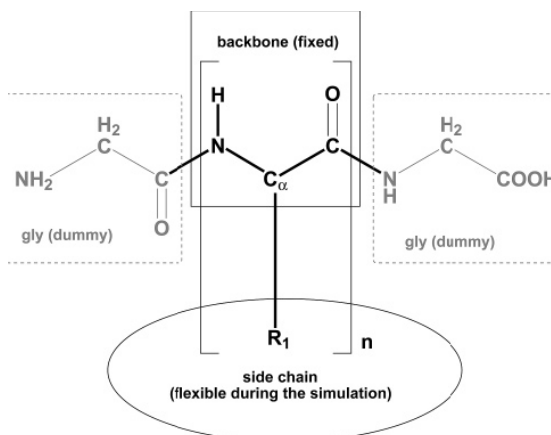


Figure 9. Structure of the system used in molecular dynamics and MCTI simulations.

Structure and Energetics of Clustered Damaged Sites

JH Miller,^(a) A Aceves-Gaona,^(a) MB Ernst,^(a) M Haranczyk,^(b) MS Gutowski,^(b) ER Vorpapel,^(c) and M Dupuis^(b)

(a) Washington State University Tri-Cities, Richland, Washington

(b) Pacific Northwest National Laboratory, Richland, Washington

(c) W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington

Computations give insight into damaged and mutated sites in DNA.

Quantum calculations on duplex DNA trimers were used to model the changes in structure, hydrogen bonding, stacking properties, and electrostatic potential induced by oxidized purine bases and abasic (AP) sites. Results for oxidized purine bases were consistent with experimental data that show small structural and energetic perturbations induced by isolated 8-oxoguanine (8oG). Watson-Crick base pairing was preserved, and no major distortions of the backbone were induced. The thermal destabilization of DNA induced by 8oG was

comparable to the energy of a single hydrogen bond. In contrast, AP sites caused substantial distortions of the DNA backbone that were accompanied by relocation of counterions. The loss of Watson-Crick hydrogen bonds in AP sites had the potential to destabilize DNA by 10–20 kcal/mol (0.4–0.8 eV); however, new inter- and intrastrand hydrogen bonds formed after removal of a nucleic acid base that significantly affected the energy of AP sites and introduced a strong dependence on sequence context. Quantum calculations on small DNA fragments provided starting conformations and force-field parameters for classical molecular dynamics simulations of radiation-induced single-strand breaks (Figure 10) that most often combine hydrolysis of a phosphate-oxygen (P-O) bond with an AP site and fully or partially degraded sugar ring. P-O bond hydrolysis increased the freedom in backbone torsion angles, which allowed the broken strand to compress and partially fill the hole in the DNA created by the AP site. Results for strand breaks with a 3'phosphoglycolate were similar to those with phosphate end groups.

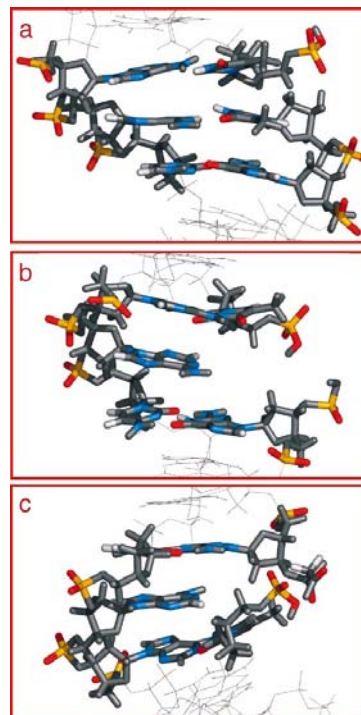


Figure 10. The effect of different type of strand breaks on the conformation of duplex DNA oligonucleotide.

Analytic Energy Gradients of the Optimized Effective Potential Method

Q Wu,^(a) AJ Cohen,^(a) and W Yang^(a)

(a) Duke University, Durham, North Carolina

A new approach to analytical gradient calculations in the optimized effective potential formulation of density functional theory can make complex molecular calculations more efficient.

The analytic energy gradients of the optimized effective potential (OEP) method in density-functional theory have been developed. Their implementation in the direct optimization approach (Yang and Wu 2002; Wu and Yang 2003) are carried out and the validity is confirmed by comparison with corresponding gradients calculated via numerical finite difference. These gradients are then used to perform geometry optimizations on a test set of molecules. Exchange-only OEP molecular geometries are found to be very close to the Hartree-Fock results and that the difference between the B3LYP and OEP-B3LYP results is negligible. When the energy is expressed in terms of a functional of Kohn-Sham orbitals, or in terms of a Kohn-Sham potential, the OEP becomes the only way to perform density-functional calculations, and the present development in the OEP method should play an important role in the applications of orbital or potential functionals.

Citations

Wu Q, and W Yang. 2003. "Algebraic Equation and Iterative Optimization for the Optimized Effective Potential in Density Functional Theory." *Journal of Theoretical and Computational Chemistry* 2(4):627-638.

Yang W, and Q Wu. 2002. "Direct Method for Optimized Effective Potentials in Density-Functional Theory." *Physical Review Letters* 89(14):143002 (pages 1-4).

Awards and Recognition

Research highlighted on the cover of the *Journal of Physical Chemistry*. The team of PNNL researchers and EMSL users Peter Lu, Dehong Hu, and Duohai Pan combined atomic force and confocal Raman microscopy techniques to follow interfacial electron transfer in a dye-sensitized semiconductor system. The new results are a significant step forward in characterizing site-specific inhomogeneous interfacial charge transfer dynamics—a process important to several fields such as chemistry, physics, and biology. The research was featured on the cover of the September 1, 2005, issue of *Journal of Physical Chemistry B*.

Imaging system success story featured on the cover of *Scientific Computing & Instrumentation*. How a team of PNNL and Utah State University scientists and programmers overcame problems with a unique microscope developed for obtaining live images and cells and proteins is the topic of a cover story in the October 2005 issue of *Scientific Computing & Instrumentation*. The story, "Pixel Perfect – A Real-Time Image Processing System for Biology," describes how a multispectral confocal microscope developed at PNNL works and how the instrument's image registration problems were solved. The team consists of EMSL researchers Derek Hopkins and Brian LaMarche; PNNL researchers Marianne Sowa and Kenneth Perrine; and Scott Budge, Utah State University. PNNL chief scientist Steven Wiley developed the microscope and the work was sponsored by PNNL's Biomolecular Systems Initiative. The article can be accessed at: <http://www.scamag.com/ShowPR.aspx?PUBCODE=030&ACCT=3000000100&ISSUE=0509&RELTYPE=PR&ORIGRELTYPE=FE&PRODCODE=00000000&PRODLETT=L>.

10th International Conference on Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere (Migration '05). On September 18 – 23, Zheming Wang attended the 10th International Conference on Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere (Migration '05) at Avignon, France. His poster presentation "A Spectroscopic and Microscopic Study of Uranium Speciation in the Infiltration Pond Sediments at Hanford, USA" (co-authors: JM Zachara, SK Shelly, JP McKinley, SC Smith, O Qafuko, and SM Heald) was co-recipient of the best poster award out of 275 poster presentations.

Eighth International Conference on Laser Ablation (COLA 05). Nikki Avery (PNNL), Ken Beck (EMSL), Alan Joly, and Wayne Hess (both PNNL) attended the Eighth International Conference on Laser Ablation (COLA 05), which was held September 11-16, 2005, in Banff, Canada. COLA was attended by more than 250 scientists from 25 countries, and it is the leading international conference in the field of laser ablation. Avery was the

conference organizer, while Hess served as conference co-chair. All four individuals were part of the local coordinating committee. The conference explores fundamentals of lasers–materials interactions and their forefront applications in pulsed laser deposition, nanoscience, analytical methods, materials science, and microprocessing applications.

Professional/Community Service

National Science Foundation Panel. David Hoyt was invited to serve as a panelist for the National Science Foundation Chemistry Research Instrumentation and Facilities-Multiuser Instrument Acquisition Panel for Fiscal Year 2006. The panel met in Arlington, Virginia, on October 27 and 28.

Major Facility Upgrades

None

News Coverage

None

Visitors and Users

Chemistry and Physics of Complex Systems Facility

- H.C. Dieter Bäuerle, Johannes Kepler Universität, Österreich, Austria, gave the seminar “Laser Processing and Chemistry: Applications in Nano-Patterning, Material Synthesis and Biotechnology.”
- Alexander I. Boldyrev, Utah State University, Logan, Utah, worked on the study “Investigation of Aromatic and Other Novel Gas Phase Atomic Clusters and Molecules.”
- Olexandr Bondarchuk, University of Texas at Austin, Texas, worked on the study “Atomically Resolved Studies of Transition Metal Oxides.”
- Ivan Chu, University of Hong Kong, Pokfulam, Hong Kong, participated in the Interfacial and Condensed-Phase Chemical Physics Summer Research Institute and worked on the study “Energetics of Dissociation of Peptide Radical Cations.”

- Tim Lian, Emory University, Atlanta, Georgia, gave the seminar “Ultrafast Electron Transfer at the Molecule-Semiconductor Nanoparticle Junctions.”
- Weigang Lu, University of New Orleans, New Orleans, Louisiana, gave the seminar “Synthesis and Self-Assembly of Low Dimensional Semiconductor Nanocrystals” and worked on the study “Early Transition Metal Oxides as Catalysts.”
- Anoop Mayampurath, Utah State University, Logan, Utah, participated in the Interfacial and Condensed-Phase Chemical Physics Summer Research Institute and worked on the study “Develop a Procedure for the Determination of the Calibration Parameters on the Host Side and Integrate Them into the Hardware to Facilitate Real Time Multiband Analysis.”
- 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.”
- Luis Rodriguez, National Cancer Institute, Bethesda, Maryland, worked on the study “Development of Multi-Functional Microscopy (MFM) for Cancer and AIDS Research.”
- Ebbe K. Vestergaard, University of Washington, Seattle, Washington, gave the seminar “Scanning Tunneling Microscopy Studies of ‘Active Sites’ on Metal and Oxide Surfaces” and worked on the study “Photochemical Studies on N-Doped TiO₂ Single Crystals.” Vestergaard is also a participant in the Joint Institute for Nanoscience and Nanotechnology.
- Peng Wang, University of California, Davis, California, gave the seminar “State-Selected and State-to-State Photoionization-Photoelectron Spectroscopy using Two-Color Vacuum Ultraviolet and Infrared Lasers.”
- Wei (David) Wei, University of Texas at Austin, Texas, participated in the Interfacial and Condensed-Phase Chemical Physics Summer Research Institute and worked on the study “Photoelectron Emission Microscopy (PEEM) Study of Cu Nanoparticles on TiO₂(110).”
- Dong-Sheng Yang, University of Kentucky, Lexington, Kentucky, gave the seminar “Spectroscopy and Bonding Modes of Transient Metal-Organic Complexes.”
- Tieqiao Zhang, National Institutes of Health, Bethesda, Maryland, worked on the study “Analysis of Lipid Nanoparticle Interaction with Cell Membrane.”
- Zhenrong Zhang, University of Texas at Austin, Texas, worked on the study “Photochemistry of Halogenated Hydrocarbon on TiO₂(110) Surface.”

Environmental Spectroscopy and Biogeochemistry Facility

- Paul Bagus, University of North Texas, Denton, Texas, along with Eugene Ilton, Pacific Northwest National Laboratory, Richland, Washington, continued their collaborations to study the effect of covalency on the x-ray photon spectroscopy of MnO as well as on the quantitative assignment of valence anti-bonding and Rydberg orbitals to the fine structure of the O K-edge x-ray absorption near-edge spectroscopy.
- Stuart Bogatko and Brigitta Elsasser (see Figure 11), University of California, San Diego, La Jolla, California, collaborated with Eric J. Bylaska, Pacific Northwest National Laboratory, Richland, Washington, and EMSL researcher Marat Valiev. Stuart Bogatko is studying high-temperature (pressure) electrolyte solutions thought to facilitate metal ion transport in hydrothermal environments by using *ab initio* molecular dynamics methods, and Dr. Elsasser is studying enzymatic reactions using quantum mechanics/molecular mechanics methods. Both researchers are using the EMSL supercomputer to perform their simulations.
- Baolin Deng, University of Missouri, Columbia, Missouri, along with Chongxuan Liu and Eugene Ilton, Pacific Northwest National Laboratory, Richland, Washington, continued their collaboration using x-ray photoelectron spectroscopy and surface complexation modeling and simulations to investigate Cr(VI) removal from waste water by a quaternized polymer-coated activated carbon.
- Hailiang Dong, Miami University, Oxford, Ohio, and EMSL researcher Ravi Kukkadapu continued their Mossbauer studies of pristine nontronite samples at low temperatures. This work is attempting to elucidate a) the effect of layer charge/aluminum-substitution on rates and extent of nontronite bioreduction, and b) identify the nature of the biotransformation product.



Figure 11. Stuart Bogatoka and Brigitta Elsasser.

- James Kubicki (Figure 12), Pennsylvania State University, University Park, Pennsylvania, gave the seminar "The Role of Solvation in Modeling Mineral Surface Complexes," in which he elaborated on his work under the joint National Science Foundation-DOE Environmental Molecular Sciences Institute grant. His work at EMSL involves collaboration with Kevin Rosso, Pacific Northwest National Laboratory, Richland, Washington, on modeling electron transfer reactions between aqueous ferrous iron and hydrated surfaces of goethite. The visit included interactions with PNNL researchers Rosso and John Zachara and EMSL researchers Theresa Windus and Bert de Jong.

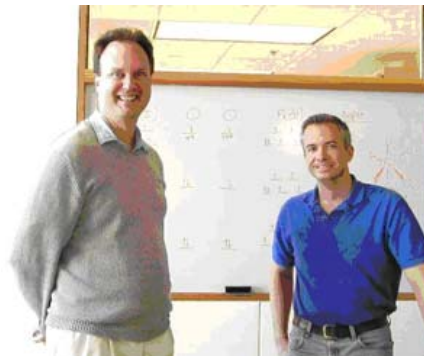


Figure 12. James Kubicki and Kevin Rosso.

- Kelly Whitaker (Figure 13), University of Washington, Seattle, Washington, is working with Jim Amonette and Alan Joly, Pacific Northwest National Laboratory, Richland, Washington, to characterize changes in the Fermi level of transition-metal-doped zinc-oxide nanoparticles. Electron paramagnetic resonance spectroscopy was used to monitor the rate of change upon exposure of the nanoparticles to ultraviolet light.



Figure 13. Kelly Whitaker and Jim Amonette.

High-Field Magnetic Resonance Facility

- Jian Zhi Hu, Charles Peden, and Yong Wang, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 900-MHz spectrometer for the study "*In-situ* High Field, High Resolution NMR Spectroscopy."
- Michael Kennedy, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 750-MHz, 600-MHz, and 500-MHz spectrometers for the study "Structural Genomics Collaborative Access Team (CAT)."
- Rachel Kleivit and Peter Brzovic, University of Washington, Seattle, Washington, worked onsite and remotely using the Cryoprobe 600-MHz spectrometers for the study "NMR Structural Investigations of BRCA1."

- Howard Lacheen and Enrique Iglesia, University of California, Berkeley, California, worked remotely using the 900-MHz spectrometer for the study “Solid State MAS NMR of High-Valent Cation Exchanged H-MFI.”
- Andrew Lipton, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 900-MHz and 800-MHz spectrometers for the study “Correlation of Structure and Function of Zinc Metalloproteins via Solid-State NMR Methods.”
- Ponni Rajagopal, University of Washington, Seattle, Washington, worked remotely using the 800-MHz, 750-MHz, and 600-MHz spectrometers for the study “Structural Investigation of alphaB-Crystallin Core Domains.”
- Raymond Reeves, Washington State University, Pullman, Washington, worked remotely using the 900-MHz spectrometer for the study “Structural Biology of the Human High Mobility Group A (HMGA) Proteins: Characterizing the Hub of Nuclear Function.”
- Celine Schneider and Richard Darton, University of British Columbia, Vancouver, British Columbia, Canada, worked onsite using the 800-MHz spectrometer for the study “Structural Investigations of Solid Materials by High Resolution Solid-State NMR at Very High Field.”
- Wendy Shaw, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 300-MHz spectrometer for the study “Draws Implementation.”
- Jianjun Wang, Jianglei Chen, and Yonghong Zhang, Wayne State University, Detroit, Michigan, worked onsite and remotely using the 900-MHz, 750-MHz, and 600-MHz Cryoprobe spectrometers for the study “NMR Studies of a 180 kDa HDL Particle.”

The following individuals sent samples to be run on the 750-MHz, 600-MHz, and 500-MHz NMR spectrometers in support of EMSL's Structural Genomics Collaborative Access Team, led by Michael Kennedy, Pacific Northwest National Laboratory, Richland, Washington:

- Cheryl Arrowsmith, University of Toronto, Toronto, Ontario, Canada
- Guy Montelione, Rutgers University, Piscataway, New Jersey.

High-Performance Mass Spectrometry Facility

- Jon Jacobs, Pacific Northwest National Laboratory, Richland Washington, worked on the study “Proteomic Characterization of Cerebrospinal Fluid (CSF) by High Resolution LC-MS/MS.” Recent collaborative work between PNNL and Massachusetts General Hospital researchers has resulted in an in-depth proteomic

characterization of human cerebral spinal fluid. More than 1,000 proteins have been detected and identified in human cerebral spinal fluid by using advanced mass spectrometry proteomic techniques, resulting in the most comprehensive coverage to date and providing a database for future comparative studies of disease model systems.

- Lee Krumholz, University of Oklahoma, Norman, Oklahoma, worked on the study “Proteome Analysis of Regulatory Gene Mutants in *Desulfovibrio Desulfuricans* G20 and *Shewanella oneidensis* MR-1.” Eighteen *Shewanella oneidensis* samples representing three biological triplicates from six locations and 27 *Desulfovibrio desulfuricans* samples representing three biological triplicates from nine locations were processed into mass spectrometric compatible peptides. The peptides are currently being detected by the 9-tesla Fourier transform ion cyclotron resonance mass spectrometer. This data will be used to identify protein changes (if any) in the various cell isolates.
- Mary Lipton, Pacific Northwest National Laboratory, Richland, Washington, worked on the study “Shew Strains.” Ten different strains of *Shewanella* have been analyzed using liquid chromatography/tandem mass spectrometry. These strains represent a large sampling of species across a genus and will help define the differences and similarities of the strains and species within the *Shewanella* species. The data have been analyzed against the *oneidensis* genome sequence, but recently the genome sequences of the organisms have been released and all the data will be analyzed against the appropriate genome sequence.
- David Springer, Pacific Northwest National Laboratory, Richland, Washington, worked on the study “Biomarker Development for Chronic Obstructive Pulmonary Disease.”
- Thomas Squier, Pacific Northwest National Laboratory, Richland, Washington, worked on the study “Genomes to Life Protein Complex Isolation Capability.” Technologies continue to be developed for high-throughput protein complex isolation and identification within the Genomes to Life project. Several hundred pull-down samples were run on the LCQ tandem mass spectrometer, and protein components of *in vitro* isolated protein components were identified. The protein interaction data will be entered into the protein interaction database for *Shewanella oneidensis* and *Rhodospseudomonas palustris* organisms of interest to DOE.
- Himadri Pakrasi, Washington University, St. Louis, Missouri, worked on the study “Grand Challenge in Membrane Biology.”
- Arzu Umar, Erasmus University Medical Center, Rotterdam, Netherlands, worked on the study “Identification of Functional Pathways Associated with Clinical Tamoxifen-Resistance in Breast Cancer by Advanced Mass Spectrometry.”

Interfacial and Nanoscale Science Facility

- Zsuzsanna Balogh, Washington State University, Pullman, Washington, used the electron microscopy suite to characterize mineral nanostructures in order to understand issues associated with soil mineral weathering.
- Chundi Cao, Kansas State University, Manhattan, Kansas, used EMSL's electron microscopy capabilities to study the influence of particle-sized distribution and the chemical composition on catalytic ignition associated with catalytic partial oxidation of hydrocarbons.
- Allen Chaparadza, Portland State University, Portland, Oregon, visited EMSL to make the determination of p-dopant concentration in a wide band gap SnO_2 semiconductor, using the Rutherford backscattering spectrometry technique.
- Ricardo Chimentao, University of Washington, Seattle, Washington, worked on understanding the mechanisms associated with the catalytic properties of $\text{Ba}(\text{NO}_3)_2$ support on gamma alumina.
- Ramana Chintalapalle, University of Michigan, Ann Arbor, Michigan, determined hydrogen depth profiles using nuclear reaction analysis in biotite minerals.
- Cynthia Dutton, University of Oregon, Eugene, Oregon, used EMSL capabilities to study the nanoscience of organometallic chemistry.
- Aaron Feaver, University of Washington, Seattle, Washington, investigated catalysts used to control the selectivity of hydrogen storage materials.
- Maxime Guinel, Washington State University, Pullman, Washington, worked on the determination of the silica polymorphs thermally grown on silicon carbide as a function of temperature and time using x-ray photoelectron spectroscopy.
- Kerstin Honer zu Bentrup, Tulane University, New Orleans, Louisiana, used EMSL's electron microscopy to observe infection of the intestinal cells with Norovirus.
- Claire Johnson and Kevin Kittilstved, University of Washington, Seattle, Washington, studied the ferromagnetic activation in ZnO diluted magnetic semiconductors.
- Sun-Ae Jun, Dongguk University, Seoul, Korea, and Sang-Mok Lee, Iha University, Incheon, Korea, studied immobilized enzymes for bioremediation and biosensing.
- Joseph Megy, JDC Inc., New Cumberland, West Virginia, worked to determine the reaction temperature and melting temperature of phosphate ore mixture. Thermal

gravimetric analysis-differential thermal analysis measurements were carried out to determine the temperature.

- Carl Seliskar, University of Cincinnati, Cincinnati, Ohio, studied chemically selective sensor film characterization.
- Chen-Luen Shih, University of Washington, Seattle, Washington, studied the properties of polysilicon grown on silicon substrate with nickel metal as a buffer layer. He is mainly using EMSL thin film sputter deposition capabilities to grow these films. He is also using EMSL x-ray diffraction, transmission electron microscopy, atomic force microscopy, and clean room capabilities that are directly associated with his research work.
- Mingyao Zhu, College of William and Mary, Williamsburg, Virginia, worked to quantify trace elements in carbon nanosheets using proton induced x-ray emission. These are free-standing two-dimensional carbon nanostructures synthesized by radio frequency plasma-enhanced chemical vapor deposition.

Molecular Science Computing Facility—New User Agreements with NWChem/Ecce

- BASF AG, Ludwigshafen am Rhein, Germany
- ClusterVision BV, Amsterdam, Netherlands
- Cornell University, Ithaca, New York
- Delft University of Technology, Delft, The Netherlands
- Delta Computer Products GmbH, Reinbek, Germany
- Department of Defense Army Research Laboratory Major Shared Resource Center, Aberdeen, Maryland
- Ente per le Nuove Tecnologie l'Energia e l'Ambiente, Frascati, Italy
- Federal University of Santa Catarina, Florianopolis, Brazil
- Fox Chase Cancer Center, Philadelphia, Pennsylvania
- Fudan University, Shanghai, China
- Humboldt University of Berlin Faculty of Agriculture and Horticulture Institute of Plant Sciences, Bernau, Germany
- IBM, Montpellier, France
- Icagen Inc., Durham, North Carolina
- Indian Institute of Information Technology and Management, Gwalior, India
- Inner Mongolia University, Huhhot, China

- Institut Pasteur, Paris, France
- Karl-Franzens Universitaet, Graz, Austria
- Korean Research Institute of Bioscience and Biotechnology, Taejon, Korea
- Megware Computer GmbH, Roehrsdorf, Germany
- Michigan State University, East Lansing, Michigan
- Nankai University, Tianjin, China
- National Research Council Institute for Fuel Cell Innovation, Vancouver, British Columbia, Canada
- Oakland University, Rochester, Michigan
- Ohio State University, Columbus, Ohio
- Peking University, Shenzhen, China
- Pennsylvania State University, University Park, Pennsylvania
- Robert J. Mears, Limited Liability Corporation, Waltham, Massachusetts
- Russian Academy of Sciences, Boreskov Institute of Catalysis, Novosibirsk, Russia
- Sandia National Laboratories, Albuquerque, New Mexico
- Shanghai Jiao Tong University, Shanghai, China
- Shared Hierarchical Academic Research Computing Network, London Ontario, Canada
- Simon Fraser University, Burnaby, British Columbia, Canada
- Stanford University, Stanford, California
- Tata Research Development an Design Centre, Pune, India
- The Chinese University of Hong Kong, Shatin, Hong Kong
- The University of Glasgow, Glasgow, Scotland
- Thomas Jefferson University, Philadelphia, Pennsylvania
- Tubitak Ulakbim, Ankara, Turkey
- Universidade de Coimbra, Coimbra, Portugal
- Universita di Cagliari, Monserrato (Cagliari), Italy
- Universite Mohammed V Agdal, Rabat, Morocco
- University of Birmingham, Birmingham, United Kingdom
- University of Colorado, Boulder, Colorado
- University of Santiago de Compostela, Santiago de Compostela, Spain
- University of Southern Indiana, Evansville, Indiana
- University of Texas at Austin, Austin, Texas

New EMSL Staff

Daniel (Dan) Corbett joined the High Performance Computing and Networking Services group. He obtained his Bachelor of Science degree in Computer Sciences from Eastern Washington University, with minor emphasis in Mathematics and Physics.

Robert (Rob) Farber joined the Molecular Science Computing Facility Operations group. He is a technical architect and leader in scaleable distributed software. He has extensive experience building clusters and file systems, and has a broad knowledge of current Unix file systems, including Lustre. Farber attended the University of Chicago, where he received honors working with Dr. Jack Cowan to model excitatory/inhibitory networks in neurobiology. He obtained his Bachelor of Science degree in Biology.

James Bradley (Brad) Mahlen joined the Instrument Development Laboratory. He is currently working towards his degree as a full-time student in the Washington State University Tri-City Engineering Program. Mahlen worked for Zetec in Issaquah for more than six years and has experience in engineering support, prototype testing, bread boarding, design, and documentation.

Surya Singh joined the High Performance Computing and Networking Services group. He has a Masters degree in Business Administration from Idaho State University, with emphasis in Information Systems and Finance. Singh has Cisco Certified Network Associate, Cisco Certified Design Associate, Microsoft Certified Systems Engineer NT 4, Windows 2000, and Certified Novell Design certifications. He is currently pursuing his Certified Information Systems Security Professional certification.

Publications

Bryantsev VS, and BP Hay. 2005. "Influence of Substituents on the Strength of Aryl C-H...Anion Hydrogen Bonds." *Organic Letters* 7(22):5031-5034.

Cannon WR, KH Jarman, BJM Webb-Robertson, DJ Baxter, CS Oehmen, KD Jarman, A Heredia-Langner, KJ Auberry, and GA Anderson. 2005. "Comparison of Probability and Likelihood Models for Peptide Identification from Tandem Mass Spectrometry Data." *Journal of Proteome Research* 4(5):1687-1698.

Cape JL, JR Strahan, MJ Linaeus, BA Yuknis, TT Le, JN Shepherd, MK Bowman, and DM Kramer. 2005. "The Respiratory Substrate Rhoquinol Induces Q-Cycle Bypass Reactions in the Yeast Cytochrome *b_c1* Complex: Mechanistic and Physiological Implications." *Journal of Biological Chemistry* 280(41):34654-34660.

Chambers SA, JR Williams, MA Henderson, AG Joly, M Varela, and SJ Pennycook. 2005. "Structure, Band Offsets and Photochemistry at Epitaxial α -Cr₂O₃/ α -Fe₂O₃ Heterojunctions." *Surface Science* 587(3): L197-L207.

- Chen W, JO Bovin, S Wang, AG Joly, Y Wang, and PMA Sherwood. 2005. "Fabrication and Luminescence of ZnS:Mn²⁺ Nanoflowers." *Journal of Nanoscience and Nanotechnology* 5(9):1309-1322.
- Choowongkomon K, CR Carlin, and FD Sonnichsen. 2005. "A Structural Model for the Membrane-Bound Form of the Juxtamembrane Domain of the Epidermal Growth Factor Receptor." *Journal of Biological Chemistry* 280(25):24043-24052.
- Dhamne A, W Xu, BG Fookes, Y Fan, L Zhang, S Burton, J Hu, J Ford, and L An. 2005 "Polymer-Ceramic Conversion of Liquid Polyaluminasilazanes for SiAlCN Ceramics." *Journal of the American Ceramic Society* 88(9):2415-2419.
- Dong J, LK Opresko, W Chrisler, G Orr, RD Quesenberry, DA Lauffenburger, and HS Wiley. 2005. "The Membrane-Anchoring Domain of Epidermal Growth Factor Receptor Ligands Dictates Their Ability to Operate in Juxtacrine Mode." *Molecular Biology of the Cell* 16(6):2984-2998.
- Elias DA, ME Monroe, MJ Marshall, MF Romine, AS Belieav, JK Fredrickson, GA Anderson, RD Smith, and MS Lipton. 2005. "Global Detection and Characterization of Hypothetical Proteins in *Shewanella oneidensis* MR-1 Using LC-MS Based Proteomics Based Proteomics." *Proteomics* 5(12):3120-3130.
- Hendriks BS, G Orr, A Wells, HS Wiley, and DA Lauffenburger. 2005. "Parsing ERK Activation Reveals Quantitatively Equivalent Contributions from Epidermal Growth Factor Receptor and HER2 in Human Mammary Epithelial Cells." *Journal of Biological Chemistry* 280(7):6157-6169.
- Iordanova N, M Dupuis, and KM Rosso. 2005. "Theoretical Characterization of Charge Transport in Chromia (α -Cr₂O₃)." *Journal of Chemical Physics* 123(7):074710 (pages 1-11).
- Ji M, X Gu, X Li, X Gong, J Li, and LS Wang. 2005. "Experimental and Theoretical Investigation of the Electronic and Geometrical Structures of the Special Au₃₂ Cluster." *Angewandte Chemie International Edition* 44(43):7119-7123.
- Laskin A, MJ Iedema, A Ichkovich, ER Graber, I Taraniuk, and Y Rudich. 2005. "Direct Observation of Completely Processed Calcium Carbonate Dust Particles." *Faraday Discussions* 130:453-468.
- Liu G, SL Riechers, MC Mellen, and Y Lin. 2005. "Sensitive Electrochemical Detection of Enzymatically Generated Thiocholine at Carbon Nanotube Modified Glassy Carbon Electrode." *Electrochemistry Communications* 7(11):1163-1169.
- Lyubinetzky I, AS Lea, S Thevuthasan, and DR Baer. 2005. "Formation of Epitaxial Oxide Nanodots on Oxide Substrate: Cu₂O on SrTiO₃(100)." *Surface Science* 589(1-3):120-128.
- Majors PD, JS McLean, GE Pinchuk, JK Fredrickson, YA Gorby, KR Minard, and RA Wind. 2005. "NMR Methods for *in situ* Biofilm Metabolism Studies." *Journal of Microbiological Methods* 62(3):337-344.

Mattigod SV, GE Fryxell, K Alford, T Gilmore, K Parker, J Serne, and M Engelhard. 2005. "Functionalized TiO₂ Nanoparticles for Use for *in situ* Anion Immobilization." *Environmental Science and Technology* 39(18):7306-7310.

McIntire TM, AS Lea, DJ Gaspar, N Jaitly, Y Dubowski, Q Li, and BJ Finlayson-Pitts. 2005. "Unusual Aggregates from the Oxidation of Alkene Self-Assembled Monolayers: A Previously Unrecognized Mechanism for SAM Ozonolysis?" *Physical Chemistry Chemical Physics: PCCP* 7(20):3605-3609.

Miller JH, A Aceves Gaona, MB Ernst, M Haranczyk, MS Gutowski, ER Vorpagel, and M Dupuis. 2005. "Structure and Energetics of Clustered Damage Sites." Chapter PT 2 in *3rd International Workshop on Space Radiation Research and 15th Annual NASA Space Radiation Health Investigators' Workshop, Port Jefferson, New York, May 16-20, 2004*, vol. 164, no. 4, pp. 582-585. Radiation Research Soc., Oak Brook.

Orr G, D Hu, S Ozcelik, LK Opresko, HS Wiley, and SD Colson. 2005. "Cholesterol Dictates the Freedom of EGF Receptors and HER2 in the Plane of the Membrane." *Biophysical Journal* 89(2):1362-1373.

Pan D, D Hu, and HP Lu. 2005. "Probing Inhomogeneous Vibrational Reorganization Energy Barriers of Interfacial Electron Transfer." *Journal of Physical Chemistry B* 109(34):16390-16395.

Perera SA, PB Rozyczko, RJ Bartlett, and S Hirata. 2005. "Improving the Performance of Direct Coupled Cluster Analytical Gradients Algorithms." *Molecular Physics* 103(15-16):2081-2083.

Perrine KA, DF Hopkins, BL LaMarche, SE Budge and MB Sowa. 2005. "Pixel Perfect – A Real-Time Image Processing System for Biology." *Scientific Computing & Instrumentation* (September 2005), <http://www.scamag.com>.

Petrik NG, and GA Kimmel. 2005. "Electron-Stimulated Sputtering of Thin Amorphous Solid Water Films on Pt(111)." *Journal of Chemical Physics* 123(5):054702 (pages 1-7).

Petrik NG, and GA Kimmel. 2005. "Low-Energy Electron-Stimulated Luminescence of Thin H₂O and D₂O Layers on Pt(111)." *Journal of Physical Chemistry B* 109(33):15835-15841.

Punnoose A, J Hays, A Thurber, MH Engelhard, RK Kukkadapu, C Wang, V Shutthanandan, and S Thevuthasan. 2005. "Development of High-Temperature Ferromagnetism in SnO₂ and Paramagnetism in SnO by Fe Doping." *Physical Review B. Condensed Matter and Materials Physics* 72(5):054402 (pages 1-14).

Rinsland CP, SW Sharpe, and RL Sams. 2005. "Temperature-Dependent Infrared Absorption Cross Sections of Methyl Cyanide (Acetonitrile)." *Journal of Quantitative Spectroscopy and Radiative Transfer* 96(2):271-280.

Shen Y, J Kim, EF Strittmatter, JM Jacobs, DG Camp II, R Fang, N Tolic, RJ Moore, and RD Smith. 2005. "Characterization of the Human Blood Plasma Proteome." *Proteomics* 5(15):4034-4045.

- Smith JA, M Josowicz, M Engelhard, DR Baer, and J Janata. 2005. "Gold-Polyaniline Composites: Part II. Effects of Nanometer Sized Particles." *Physical Chemistry Chemical Physics: PCCP* 7(20):3619-3625.
- Springer DL, M Ahram, JN Adkins, LE Kathmann, and JH Miller. 2005. "Characterization of Medium Conditioned by Irradiated Cells Using Proteome-Wide, High-Throughput Mass Spectrometry." *Radiation Research* 164(5):651-654.
- Tait SL, Z Dohnalek, CT Campbell, and BD Kay. 2005. "Methane Adsorption and Dissociation and Oxygen Adsorption and Reaction with CO on Pd Nanoparticles on MgO(100) and on Pd(111)." *Surface Science* 591(1-3):90-107.
- Thomas BS, NA Marks, LR Corrales, and R Devanathan. 2005. "Threshold Displacement Energies in Rutile TiO₂: A Molecular Dynamics Simulation Study." *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 239(3):191-201.
- Tsai P, JM Marra, S Pou, MK Bowman, and GM Rosen. 2005. "Is there Stereoselectivity in Spin Trapping Superoxide by 5-*tert*-Butoxycarbonyl-5-methyl-1-pyrroline N-oxide?" *Journal of Organic Chemistry* 70(18):7093-7097.
- Wan J, TK Tokunaga, E Brodie, Z Wang, Z Zheng, D Herman, TC Hazen, MK Firestone, and SR Sutton. 2005. "Reoxidation of Bio-reduced Uranium under Reducing Conditions." *Environmental Science and Technology* 39(16):6162-6169.
- Wang CM, V Shutthanandan, S Thevuthasan, and G Duscher. 2005. "Direct Imaging of Quantum Antidots in MgO Dispersed with Au Nanoclusters." *Applied Physics Letters* 87(15):153104 (pages 1-3).
- Wang XB, B Dai, HK Woo, and LS Wang. 2005. "Intramolecular Rotation through Proton Transfer: [Fe(^η5-C₅H₄CO₂)₂] versus [(^η5-C₅H₄CO₂)Fe(^η5-C₅H₄CO₂H)]." *Angewandte Chemie International Edition* 44(37):6022-6024.
- Wang XB, HK Woo, B Kiran, and LS Wang. 2005. "Observation of Weak C-H...O Hydrogen Bonding to Unactivated Alkanes." *Angewandte Chemie-International Edition* 44(31):4968-4972.
- Wang XB, HK Woo, and LS Wang. 2005. "Vibrational Cooling in a Cold Ion Trap: Vibrationally Resolved Photoelectron Spectroscopy of Cold C₆₀ Anions." *Journal of Chemical Physics* 123(5):051106 (pages 1-4).
- Webb-Robertson BJM, DF Lowry, KH Jarman, SJ Harbo, QR Meng, AF Fuciarelli, JG Pounds, and KM Lee. 2005. "A Study of Spectral Integration and Normalization in NMR-Based Metabonomic Analyses." *Journal of Pharmaceutical and Biomedical Analysis* 39(3-4):830-836.
- Williams KH, D Ntarlagiannis, LD Slater, A Dohnalkova, SS Hubbard, and JF Banfield. 2005. "Geophysical Imaging of Stimulated Microbial Biomineralization." *Environmental Science and Technology* 39(19):7592-7600.

Wunschel DS, EA Hill, JS McLean, K Jarman, YA Gorby, N Valentine, and K Wahl. 2005. "Effects of Varied pH, Growth Rate and Temperature Using Controlled Fermentation and Batch Culture on Matrix Assisted Laser Desorption/Ionization Whole Cell Protein Fingerprints." *Journal of Microbiological Methods* 62(3):259-271.

Yantasee W, LA Deibler, GE Fryxell, C Timchalk, and Y Lin. 2005. "Screen-Printed Electrodes Modified with Functionalized Mesoporous Silica for Voltammetric Analysis of Toxic Metal Ions." *Electrochemistry Communications* 7(11):1170-1176.

Yantasee W, C Timchalk, KK Weitz, DA Moore, and Y Lin. 2005. "Optimization of a Portable Microanalytical System to Reduce Electrode Fouling from Proteins Associated with Biomonitoring of Lead (Pb) in Saliva." *Talanta* 67(3):617-624.

Zhai HJ, B Kiran, B Dai, J Li, and LS Wang. 2005. "Unique CO Chemisorption Properties of Gold Hexamer: $Au_6(CO)_n^-$ ($n=0-3$)." *Journal of the American Chemical Society* 127(34):12098-12106.

Zhang J, F Su, W Chen, R Sammynaiken, SL Westcott, DE McCready, G Li, and AG Joly. 2005. "Synthesis and Luminescence of ZnMgS:Mn²⁺ Nanoparticles." *Journal of Nanoscience and Nanotechnology* 5(9):1465-1471.

Zhang Y, J Lian, CM Wang, W Jiang, RC Ewing, and WJ Weber. 2005. "Ion-Induced Damage Accumulation and Electron-Beam-Enhanced Recrystallization in SrTiO₃." *Physical Review B, Condensed Matter and Materials Physics* 72(9):094112 (pages 1-8).

Zhang Y, WJ Weber, DE McCready, DA Grove, J Jensen, and G Possnert. 2005. "Experimental Determination of Electronic Stopping for Ions in Silicon Dioxide." *Applied Physics Letters* 87(10):104103 (pages 1-3).

Presentations

Adkins JN, AD Norbeck, SO Purvine, HM Mottaz, T Clauss, NP Manes, J Rue, J Gustin, S Wong, F Heffron, and RD Smith. 2005. "Proteomics of Bacterial and Viral Intracellular Pathogens." Presented by Joshua N. Adkins (Invited Speaker) at Texas A&M University Workshop, Richland, Washington, on September 7, 2005.

Baer DR. 2005. "Enhancing the Quality and Extending the Applicability of AES and XPS." Presented by Don Baer (Invited Speaker) at the 11th European Conference on Applications of Surface and Interface Analysis 2005, Vienna, Austria, on September 27, 2005.

Baer DR, MH Engelhard, CM Wang, KH Pecher, RL Penn, PG Tratnyek, Y Qiang, DE McCready, JC Linehan, JE Amonette, and J Antony. 2005. "Multi-Technique Characterization of Iron Nanoparticles." Presented by D. R. Baer at the American Vacuum 52nd International Symposium and Exhibition, Boston, Massachusetts, on October 30, 2005.

Beliaev AS, MJ Marshall, YA Gorby, DW Kennedy, A Dohnalkova, and JK Fredrickson. 2005. "Biomolecular Mechanisms of Fe(III) Reduction by *Shewanella oneidensis* MR-1." Presented by Alexander S. Beliaev (Invited Speaker) at collaborative research meetings/discussions, Milwaukee, Wisconsin, on October 6, 2005.

Cai Y, AN Zelenyuk, and DG Imre. 2005. "A High Resolution Study of the Effect of Morphology on the Mass Spectra of Single PSL Particles with Na-Containing Nanolayers and Nanonodules." Presented by Yong Cai at the American Association for Aerosol Research 24th Annual Meeting, Austin, Texas, on October 17, 2005.

Chambers SA. 2005. "Fundamental Investigations of Candidate Ferromagnetic Oxide Semiconductors." Presented by Scott A. Chambers (Invited Speaker) at the University of California-Santa Barbara Materials Department, Santa Barbara, California, on October 28, 2005.

Chambers SA, TC Kaspar, TC Droubay, SM Heald, CM Wang, V Shutthanandan, S Thevuthasan, DE McCready, JE Jaffe, DJ Bryan, DR Gamelin, AJ Freeman, L Ye, and AJ Kellock. 2005. "New Insights into the Mechanism(s) of Magnetism Doped TiO₂ Anatase." Presented by Scott Chambers at the 12th International Workshop on Oxide Electronics, Cape Cod, Massachusetts, on October 3, 2005.

Cho HM, WA De Jong, CZ Soderquist, BK McNamara, I Farnan, and WJ Weber. 2005. "NMR Spectroscopy of Radioactive Samples: When No Other Method Will Do." Presented by Herman Cho (Invited Speaker) at Solid State NMR of Nuclear-Related Materials: Towards Radioactive MASNMR, Cambridge, United Kingdom, on September 22, 2005.

Devanathan R, LR Corrales, WJ Weber, A Chartier, and C Meis. 2005. "Computer Simulation of Energetic Recoils in Zircon." Presented by Ram Devanathan at the 6th Pacific Rim Conference on Ceramic and Glass Technology, Maui, Hawaii, on September 15, 2005.

Devanathan R, and WJ Weber. 2005. "Computer Simulation of Radiation Effects in Gd₂Ti₂O₇ and Gd₂Zr₂O₇." Presented by Ram Devanathan (Invited Speaker) at the 6th Pacific Rim Conference on Ceramic and Glass Technology, Maui, Hawaii, on September 12, 2005.

Diamond DL, JM Jacobs, EY Chan, MA Gritsenko, S Proll, DG Camp II, RL Carithers, Jr., RD Smith, and MG Katze. 2005. "Proteomics of Hepatitis C: Comparative Studies of Liver Biopsies Reveal Protein Expression Changes Associated with Fibrosis Progression." Presented by Deborah Diamond at the 56th Annual Meeting of the American Association for the Study of Liver Diseases, San Francisco, California, on November 11, 2005.

Dohnalek Z, OA Bondarchuk, J Kim, M White, and BD Kay. 2005. "Structure and Catalytic Activity of WO₃ Clusters on TiO₂(110)." Presented by Zdenek Dohnalek (Invited Speaker) at the American Chemical Society Meeting, Washington DC, on September 1, 2005.

Engelhard MH, DR Baer, and DJ Gaspar. 2005. "Information Needed for Improving Sputter Depth Profiling." Presented by Mark Engelhard at the American Vacuum Society 52nd International Symposium and Exhibition, Boston, Massachusetts, on October 31, 2005.

Floss C, FJ Stadermann, A Nguyen, E Zinner, and AS Lea. 2005. "High Fe Contents in Presolar Silicate Grains: Primary Feature or the Result of Secondary Processing?" Presented by C. Floss at MetSoc 2005, 68th Annual Meteoritical Society, Gatlinburg, Tennessee, on September 12, 2005.

Gaspar DJ, AS Lea, DL Baer, and MH Engelhard. 2005. "Examining Ion Sputtering of Nanoparticles and Nanoporous Materials." Presented by Daniel J. Gaspar (Invited Speaker) at the 15th International Conference on Secondary Ion Mass Spectrometry, Manchester, United Kingdom, on September 13, 2005.

Henderson MA. 2005. "Photocatalysis on Single Crystal TiO₂." Presented by Michael A Henderson (Invited Speaker) at the 2005 Meeting on Condensed Phase and Interfacial Molecular Science, Warrenton, Virginia, on October 23, 2005.

Hess WP, KM Beck, and AG Joly. 2005. "Laser Induced Reactions in Solid and at Surfaces." Presented by Wayne P. Hess at the 2005 Meeting on Condensed Phase and Interfacial Molecular Science, Warrenton, Virginia, on October 21, 2005.

Jiang W, WJ Weber, CM Wang, JS Young, LA Boatner, J Lian, L Wang, and RC Ewing. 2005. "Cadmium Nanoparticles and Nanowires on Ion-Cut Surfaces." Presented by Weilin Jiang at the 2005 Symposium of the Pacific Northwest Chapter of the American Vacuum Society, Troutdale, Oregon, on September 15, 2005.

Johnson KS, BM Zuberi, L Molina, MJ Molina, A Laskin, JP Cowin, MJ Iedema, DJ Gaspar, and CM Wang. 2005. "Characterization and Atmospheric Processing of Soot Aerosols in the Mexico City Metropolitan Area." Presented by Jim Cowin (Invited Speaker) at the Gordon Conference: Atmospheric Chemistry, Big Sky, Montana, on September 7, 2005.

Kay BD, RS Smith, Z Dohnalek, and JL Daschbach. 2005. "Chemical Kinetics and Dynamics at Interfaces Structure and Reactivity of Ices, Oxides, and Amorphous Materials." Presented by Bruce D. Kay (Invited Speaker) at the 2005 Meeting on Condensed Phase and Interfacial Molecular Science, Warrenton, Virginia, on October 24, 2005.

Kimmel GA, and NG Petrik. 2005. "Non-Thermal Reactions at Surfaces and Interfaces." Presented by Greg Kimmel at the 2005 Meeting on Condensed Phase and Interfacial Molecular Science, Warrenton, Virginia, on October 24, 2005.

Kimmel GA, NG Petrik, Z Dohnalek, and BD Kay. 2005. "The Growth of Thin Water Films on a Hydrophobic Water Monolayer on Pt(111)." Presented by Greg A. Kimmel (Invited Speaker) at the American Vacuum Society 52nd International Symposium and Exhibition, Boston, Massachusetts, on October 31, 2005.

Laskin A. 2005. "Analysis of Individual Particles Using Modern Methods of Electron Microscopy and X-ray Microanalysis." Presented by Alex Laskin (Invited Speaker) at Colloquium Spectroscopicum Internationale XXXIV, Antwerp, Belgium, on September 5, 2005, and at the 15th Annual Quality Assurance Conference, Dallas, Texas, on October 18, 2005.

Lea AS, J Kim, and JW Grate. 2005. "Impact of Composite Shell Thickness on Stability of Single Enzyme Nanoparticles." Presented by Scott Lea at the American Vacuum Society 52nd International Symposium and Exhibition, Boston, Massachusetts, on October 31, 2005.

Lu HP. 2005. "Single-Molecule Electron Transfer Dynamics." Presented by Peter Lu (Invited Speaker) at the 230th American Chemical Society National Meeting, Washington DC, on September 1, 2005.

Lu HP. 2005. "Single-Molecule Kinetics and Dynamics in the Condensed Phase and at Interfaces." Presented by H. Peter Lu (Invited Speaker) at the 2005 Meeting on Condensed Phase and Interfacial Molecular Science, Warrenton, Virginia, on October 25, 2005.

Lu HP. 2005. "Single-Molecule Protein-Protein Dynamic Recognition in Cell Signaling." Presented by H. Peter Lu (Invited Speaker) at the 230th American Chemical Society National Meeting, Washington DC, on September 1, 2005.

Majors PD, JS McLean, CF Wend, RA Wind, J Costerton, and W Shi. 2005. "NMR Microscopy for the *in situ* Examination of Bacterial Physiology." Presented by Paul D. Majors (Invited Speaker) at the Philips Oral Healthcare Biofilm Symposium, Los Angeles, California, on October 25, 2005.

Moruzzi G, I Kleiner, RL Sams, SW Sharpe, and JT Hougen. 2005. "Rotational Assignment of the Highly Fractionated C=O Stretching Fundamental of CH₃CHO." Presented by Jon T. Hougen (Invited Speaker) at High Resolution Molecular Spectroscopy 19th Colloquium, Salamaca, Spain, on September 12, 2005.

Ozensoy E, J Szanyi, and CH Peden. 2005. "Model Catalyst Studies for a Molecular Understanding of NO_x-Storage-Reduction Catalysts: NO₂ and H₂O Adsorption on θ -Al₂O₃/NiAl(100)." Presented by Emrah Ozensoy at the 2005 Symposium of the Pacific Northwest Chapter of the American Vacuum Society, Troutdale, Oregon, on September 15, 2005.

Pan D, D Hu, and HP Lu. 2005. "Correlated Far-Field and Near-Field Raman Microscopy and AFM Studying Interfacial Electron Transfer of Dye-Sensitized Nanoparticles." Presented by Peter Lu (Invited Speaker) at the Nanoscale Science and Technology Workshop 2005, Seattle, Washington, on September 21, 2005.

Perrin AM, H Burger, J Demaison, F Willaert, T Masiello II, TA Blake, JE Marenich, and JE Boggs. 2005. "High Resolution Infrared Study of the ν_4 and $2\nu_9$ Bands of 11BF₂OH and 10BF₂OH: Evidence of Large Amplitude Effects for the OH-Torsion-Bending Modes in

the 92 and 41 States.” Presented by Agnes Perrin at University of Paris, Salamanca, Spain, on September 13, 2005.

Petrik NG, AG Kavetski, and GA Kimmel. 2005. “Electron-Stimulated Production of Molecular Oxygen in Thin Films of Amorphous Solid Water on Pt(111).” Presented by Nikolay Petrik (Invited Speaker) at the American Vacuum Society 52nd International Symposium and Exhibition, Boston, Massachusetts, on October 31, 2005.

Posselt M, and F Gao. 2005. "Atomistic Study of the Mobility of Small Interstitial Clusters in Silicon." Presented by M. Posselt at Gettering and Defect Engineering in Semiconductor Technology, Giens, France, on September 28, 2005.

Saraf L, V Shutthanandan, CM Wang, S Azad, OA Marina, Y Zhang, DW Matson, DE McCready, AA El-Azab, JE Jaffe, MH Engelhard, DR Baer, CH Peden, and S Thevuthasan. 2005. "Oxygen Transport in Epitaxial and Nanocrystalline Ceria-Zirconia Based Electrolytes." Presented by Lax Saraf at the 2005 Symposium of the Pacific Northwest Chapter of the American Vacuum Society, Troutdale, Oregon, on September 16, 2005.

Shutthanandan V, S Thevuthasan, TC Droubay, TC Kaspar, and SA Chambers. 2005. "Quantification of Magnetic Dopant Concentrations in Room Temperature Ferromagnetic Materials using Ion Beam Techniques." Presented by V. Shutthanandan at the 2005 Symposium of the Pacific Northwest Chapter of the American Vacuum Society, Troutdale, Oregon, on September 16, 2005.

Stadermann FJ, C Floss, E Zinner, A Nguyen, and AS Lea. 2005. "Auger Spectroscopy as a Complement to Nanosims Studies of Presolar Materials." Presented by F.J. Stadermann at MetSoc 2005, 68th Annual Meteoritical Society, Gatlinburg, Tennessee, on September 12, 2005.

Sushko PV, PE Trevisanutto, AL Shluger, KM Beck, M Henyk, AG Joly, and WP Hess. 2005. “Mechanisms of Laser-Induced Desorption of Ionic Surfaces.” Presented by Wayne Hess (Invited Speaker) at Argonne National Laboratory, Argonne, Illinois, on October 17, 2005.

Szanyi J. 2005. "Fundamental Studies on BaO/Al₂O₃-Based NO_x Storage Materials." Presented by Janos Szanyi (Invited Speaker) at the University of California at Berkeley, California, on October 6, 2005.

Teegarden JG, C Timchalk, L Wiester, A Gutowska, KM Waters, SK Sundaram, AR Willse, RA Corley, TJ Weber, G Orr, and JG Pounds. 2005. “A Multi-Disciplinary Bio-Computational Approach for Assessing the Safety of Inhaled Nanoparticles.” Presented by Justin Teegarden at the 2nd Nanotechnology and Occupational Health Conference, Minneapolis, Minnesota, on October 3, 2005.

Valentine NB, TJ Johnson, KL Wahl, KH Jarman, CE Petersen, DS Wunschel, and SW Sharpe. 2005. “Identification of Bacillus Spores Cultured on Different Media.” Presented by Nancy B. Valentine at Bacillus-ACT Conference, Santa Fe, New Mexico, on September 26, 2005.

Zachara JM. 2005. "Reductive Biogeochemistry of Iron: From Cytochromes to Aquifer Systems." Presented by John M. Zachara (Invited Speaker) at the Center for Environmental Kinetic Analysis All Hands 1st Annual Meeting, State College, Pennsylvania, on September 15, 2005.

Zhang Y, L Saraf, V Shutthanadan, KD Hughes, and S Thevuthasan. 2005. "Study of Hydrogen Stability in Low-k Dielectric Films by Ion Beam Techniques." Presented by Yanwen Zhang at the 2005 Symposium of the Pacific Northwest Chapter of the American Vacuum Society, Troutdale, Oregon, on September 16, 2005.

Zubkov T, RS Smith, Z Dohnalek, and BD Kay. 2005. "The Effect of Incident Collision Energy on the Phase, Crystallization Kinetics, and Porosity of Vapor Deposited Amorphous Solid Water Films." Presented by Tykhon Zubkov (Invited Speaker) at the 2005 Symposium of the Pacific Northwest Chapter of the American Vacuum Society, Troutdale, Oregon, on September 15, 2005, and at the American Vacuum Society 52nd International Symposium and Exhibition, Boston, Massachusetts, on October 31, 2005.