



EMSL Quarterly Highlights Report
4th Quarter, Fiscal Year 2009
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EMSL—the Environmental Molecular Sciences Laboratory—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 and expertise.

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

Research Highlights

Biological Interactions and Dynamics

Proteomic Investigation of the Time Responses of RAW 264.7 Macrophages to Infection with *Salmonella enterica*

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*EMSL researchers and users from Pacific Northwest National Laboratory and Oregon Health Sciences University applied a novel global proteomic approach to better understand the extent to which macrophages respond to infection by a form of *Salmonella*. Recognized as the first global proteomic analyses of time course responses of mouse macrophages to *S. enterica* serotype Typhimurium (*S. Typhimurium*) infection, the study may lead to new strategies for diagnosing, treating, and vaccinating against infectious disease.*

Macrophages, from the Greek for "eating cells," are white blood cells that act as cellular scavengers by ingesting dying and invading bacterial cells, but they recognize and refuse to eat their own kind. The macrophages swallow the bacterial cells and then release powerful anti-bacterials that prevent bacteria from further dividing and infecting host cells. *S. Typhimurium*, which can be transmitted by ingesting contaminated food or water, is a pathogen that grows in the gastrointestinal tract of many animal species.

By infecting susceptible mouse macrophages with *S. Typhimurium* and using global proteomics to analyze the proteins at various time points following infection, researchers identified 1,006 macrophage proteins (Figure 1). The peptide abundances of 244 macrophage proteins, or 24 percent of the total macrophages identified, changed significantly after infection. The functions of the *Salmonella*-affected macrophage proteins were diverse, including production of antibacterial nitric oxide, production of prostaglandin H₂, and regulation of intracellular traffic. The diversity in functions demonstrated a global macrophage response to *Salmonella* infection.

The researchers used Western Blot analysis to confirm the proteomic results. The analysis also revealed that *Salmonella* infection increases mitochondrial abundance of the enzyme superoxide dismutase and decreases the abundance of the sorting nexin protein SNX6, most likely through the bacterial virulence factor SopB. Superoxide dismutase acts like a natural antioxidant, repairing cells and reducing the damage caused by superoxide. Sorting nexin proteins help cells move proteins to the correct location within the endomembrane system.

Macrophages are critical in autoimmune diseases such as rheumatoid arthritis, diabetes, and multiple sclerosis. They also play a role in HIV infection and can stimulate cancer cells. Researchers gain valuable information about the strengths and weaknesses of our immune system using mouse cell models such as used here. This study leads to a better understanding of macrophage responses to infection, provides insight into disease development, and suggests targets for therapeutic intervention.

Salmonella-infected macrophages are regularly used to show the molecular mechanisms essential for the interaction between macrophage and intracellular pathogens. Macrophages are important in controlling *Salmonella*-mediated systemic infection in susceptible mice. They also help control morbidity and mortality in unvaccinated infected mice, while helping eliminate *S. Typhimurium* in vaccinated mice.

Using a liquid chromatography-mass spectrometry proteomic approach, the researchers analyzed the time course responses of the cell lysate of mouse RAW 264.7 macrophages after infection with *S. Typhimurium*. They studied samples collected at four different time points following infection (0, 2, 4, and 24 hours). Future work will focus on understanding the roles of *Salmonella*-affected macrophage proteins that could lead to improved host-based therapeutics to intracellular pathogens.

This work was supported by the Laboratory Directed Research and Development program at PNNL and the National Institute of Allergy and Infectious. The research was featured in *Infection and Immunity*.

Citation:

Shi L, SM Chowdhury, HS Smallwood, H Yoon, HM Mottaz-Brewer, AD Norbeck, JE McDermott, TRW Clauss, F Heffron, RD Smith, and JN Adkins. 2009. "Proteomic Investigation of the Time Responses of RAW 264.7 Macrophages to Infection with *Salmonella enterica*." *Infection and Immunity* 77(8):3227-3233

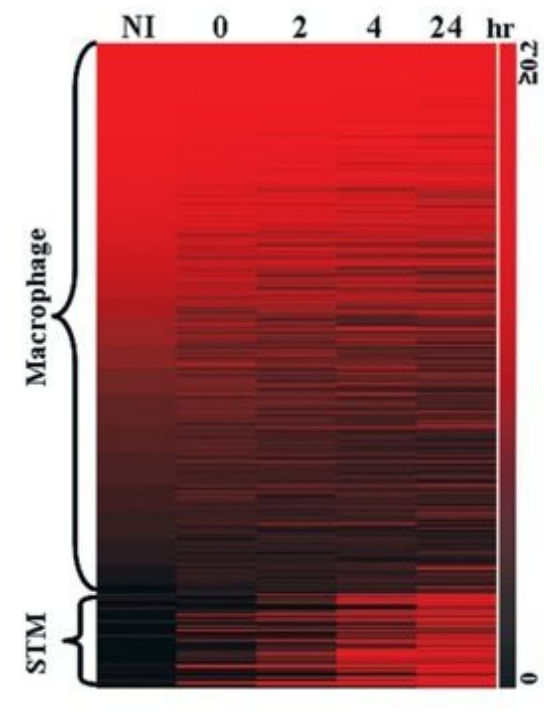


Figure 1. Peptide abundances of all identified macrophage and *S. Typhimurium* (STM) proteins. A total of 1121 proteins are shown, which include 1006 macrophage and 115 STM proteins. Peptide abundances for all identified macrophage and STM proteins in the non-infection (NI) control and at different time points of infection are indicated by colors that range from black (peptide abundance = 0%) to red (peptide abundance $\geq 0.2\%$).

Geochemistry/Biogeochemistry and Subsurface Science

Reduction of Hg(II) to Hg(0) by Magnetite

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Mercury was spilled and released as waste to the soil and groundwater at nuclear weapons production sites. In sediments with low levels of oxygen, bacteria can add a methyl group to the mercury, creating the neurotoxic substance methylmercury. To understand the formation of methylmercury, scientists need accurate information from this and related studies on the geochemistry of mercury.

Used in separating isotopes at U.S. nuclear weapons production sites, tons of mercury were released to the soil and groundwater. In anoxic or low-oxygen sediments, bacteria transform this silvery element when in the form of Hg(II) into a neurotoxin by adding a methyl group (-CH₃). The resulting methylmercury is a potent neurotoxic substance that accumulates in fish, which are harvested for food.

In a recent study, published in *Environmental Science & Technology* and highlighted in *Science*, researchers from Rutgers University, EMSL, and Pacific Northwest National Laboratory showed that a simple iron mineral transforms Hg(II) to gaseous Hg(0). The mineral known as magnetite or Fe(II)/Fe(III) mixed valence iron oxide turns Hg(II) into Hg(0) in just minutes. Subsurface bacteria cannot add a methyl group to the gaseous mercury, so it does not become the neurotoxic methylmercury (Figure 1).

The researchers conducted kinetic experiments at Rutgers University. These experiments showed that the Hg(II) gains electrons within minutes of entering an environment with magnetite. At EMSL, the scientists did Mössbauer spectroscopic analysis of reacted magnetite samples. The analysis revealed decreased Fe(II) in the magnetite. This decrease corresponds to the oxidation of Fe(II) to Fe(III) coupled to the reduction of Hg(II) to Hg(0). Finally, they used X-ray photoelectron spectroscopy to detect Hg(II) on magnetite surfaces. This analysis implied that adsorption is involved in the electron transfer process.

The results of these analysis suggest that the reaction of Hg(II) with the Fe(II)-containing oxide is a favorable pathway. This research helps scientists understand and eventually control the creation of toxic methyl mercury. This research suggests that mineral-associated processes, such as adsorption and phase

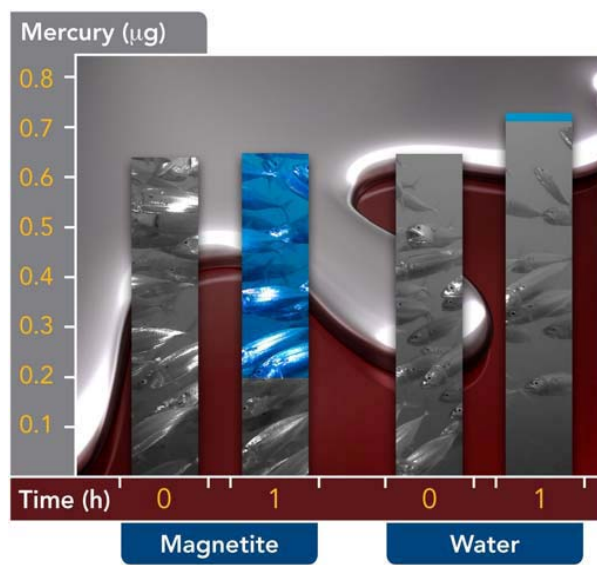


Figure 1. Magnetite reduces the amount of mercury in solution. This transformation makes the mercury unavailable for conversion by bacteria to a toxin.

transformation, may provide stiff competition in mediating mercury's fate and mobility. This research was funded by DOE's Office of Biological and Environmental Research's Environmental Remediation Sciences Program.

Citation:

Wiatrowski HA, S Das, R Kukkadapu, ES Ilton, T Barkay, and N Yee. 2009. "Reduction of Hg(II) to Hg(0) by Magnetite." *Environmental Science & Technology* 43(14):5307-5313. DOI: 10.1021/es9003608

Oxidative Dissolution Potential of Biogenic and Abiogenic TcO₂ in Subsurface Sediments

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Subsurface contaminants such as ⁹⁹Tc pose serious health risks. A study conducted by EMSL users and researchers helps provide a better understanding of the biogeochemical processes influencing the fate and transport of ⁹⁹Tc and may lead to better predictions of its migration in the subsurface and new insights into remediation strategies at nuclear facilities worldwide.

Technetium-99 is a metal formed during nuclear reactions and can be released into the environment during nuclear fuels reprocessing. It is highly mobile in its most oxidized state, Tc(VII), and much less mobile in its reduced state, Tc(IV). Technetium contamination of groundwater is a chief concern at the Department of Energy's Hanford Site, where ⁹⁹Tc has leaked from nuclear waste storage tanks to depths of 60 meters in the vadose zone, which is the region above the water table. Using resources at the DOE's EMSL, researchers found that ⁹⁹Tc in natural subsurface sediments that has been reduced by Fe(II) associated with certain mineral phases may be exceedingly resistant to oxidation and, therefore, remobilization.

The research team, comprising scientists from Pacific Northwest National Laboratory and Argonne National Laboratory, examined two sediments that differed in mineralogy and aggregation state. One was obtained from the upper Ringold Formation near the Hanford Site and the other from the Field Research Center (FRC) at the Oak Ridge Site. Both sediments contained Fe(III) and Mn(III/IV) as redox active phases, although the FRC sediment also contained different Fe-phyllsilicates minerals. The researchers used a *Shewanella*, a metal-reducing bacterium, to reduce manganese and iron oxides in the sediments. Iron in the bioreduced sediments, in turn, reduced Tc(VII) to Tc(IV). During the subsequent oxidation phase, the researchers measured Tc release from the sediments and found that Tc(IV) in the Ringold Formation sediment was oxidized and released much more rapidly and extensively than in the FRC sediment. The researchers used tools at EMSL and the Advanced Photon Source at Argonne National Laboratory to characterize sediment-associated ⁹⁹Tc and then used EMSL's X-ray microprobe, electron microprobe, X-ray absorption spectroscopy, and micro X-ray diffraction to analyze the FRC sediment and Tc-containing particles isolated from the sediment (Figure 1). These analyses revealed an oxidation-resistant Tc(IV) phase that exists with Fe(III) within iron-containing micas in the FRC sediment. The mica particles were a mineral phase called celadonite.

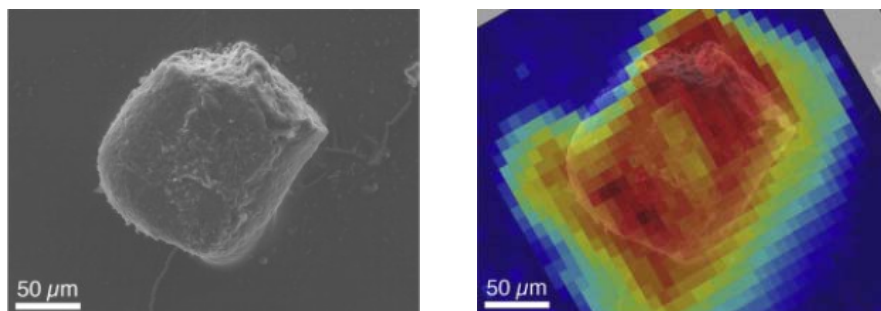


Figure 1. ⁹⁹Tc-containing particle isolated from oxidized FRC sediment: backscattered electron micrograph (left) and electron microprobe energy dispersive X-ray analysis (right).

This work offers insights into electron exchange at the microbe-mineral interface and its effect on the fate and transport of subsurface contaminants. This research was performed as part of EMSL's Biogeochemistry Grand Challenge and was supported by DOE's Office of Biological and Environmental Research Program. It was featured in *Geochimica et Cosmochimica Acta*.

Citation:

Fredrickson JK, JM Zachara, AE Plymale, SM Heald, JP McKinley, DW Kennedy, C Liu, and P Nachimuthu. 2009. "Oxidative Dissolution Potential of Biogenic and Abiogenic TcO₂ in Subsurface Sediments." *Geochimica et Cosmochimica Acta* 73(8):2299-2313.

Science of Interfacial Phenomena

Co-Ordinatively Unsaturated Al³⁺ Centers as Binding Sites for Active Catalyst Phases on γ -Al₂O₃

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Catalysts convert useless or unwanted chemicals into useful or more desirable ones. Research reported in Science reveals new, important details about a common catalyst: how rafts of chemically reactive platinum form in the catalyst. The new work yields insights into how to improve the industrial catalyst for oil refining, chemicals processing and environmental uses.

The study shows that aluminum atoms in the supporting material thirsty for another bond grab and anchor platinum (Figure 1). The anchors allow platinum atoms to group into rafts that float above the supporting surface, providing ample space for catalytic reactions.

EMSL users in the Institute for Interfacial Catalysis at Pacific Northwest National Laboratory and at Oak Ridge National Laboratory performed the analysis of the industrial catalyst known as aluminum oxide-supported platinum. Such precious metal and oxide combinations are the most common kinds of industrial catalysts. The new work will help engineers control the preparation of the catalyst, which will lead to performance improvements.

The research team has been able to specifically identify an important site for the anchoring of platinum on the aluminum oxide surface that's formed during synthesis. Although platinum rafts have been observed before, this is the first time the team has had a clear molecular-level view of the processes that create them.

In these catalysts, the oxides are merely a surface on which the precious metals sit while the metals break and form bonds in other molecules, such as those found in automobile exhaust. The most efficient catalysts spread the precious metals evenly over the surface of the oxide. Inefficient ones have precious metal atoms balled up in clumps, with the interior atoms unavailable to do their job on incoming molecules. Chemists working with gamma-aluminum oxide supports and platinum metal knew that under some conditions, rafts of platinum atoms could form on the oxide surface. Unlike balls of atoms, rafts present most of their resident atoms to incoming molecules, making them desirable structures. But to control production of the rafts, the team had to learn how they formed.

To find out, the team used powerful instruments at EMSL and the High Temperature Materials Laboratory at ORNL. The team prepared gamma-aluminum oxide under typical catalyst synthesis conditions and examined the supporting material before and after adding platinum.

First, they examined the chemical nature of the support using EMSL's 900-megahertz NMR spectrometer. The NMR provided unprecedented resolution of the aluminum oxide support, which allowed the team to identify aluminum atoms with certain properties. By their chemical nature, aluminum atoms prefer to be bound to either four or six atoms. The team found, in the absence of platinum, that some were bound to an uncomfortable five. Adding platinum to the mix, however, caused the number of aluminum atoms with five bonds to decrease, and the number of atoms with six bonds to increase. The number of four-bonded atoms stayed constant, suggesting that platinum atoms anchor at sites with come-hither, five-bonded aluminum atoms, so-called penta sites. The team found they could increase the number of penta sites by raising the temperature during catalyst synthesis. More penta sites meant more platinum atoms bound to the support.

Having found anchor points, the team zoomed in with the JEOL 2200FS aberration-corrected microscope, which could discern individual platinum atoms, at HTML. At low concentrations of the metal, individual platinum atoms showed up as bright spots scattered across the dark surface. At higher concentrations, the telltale image of platinum rafts could be seen above the aluminum oxide.

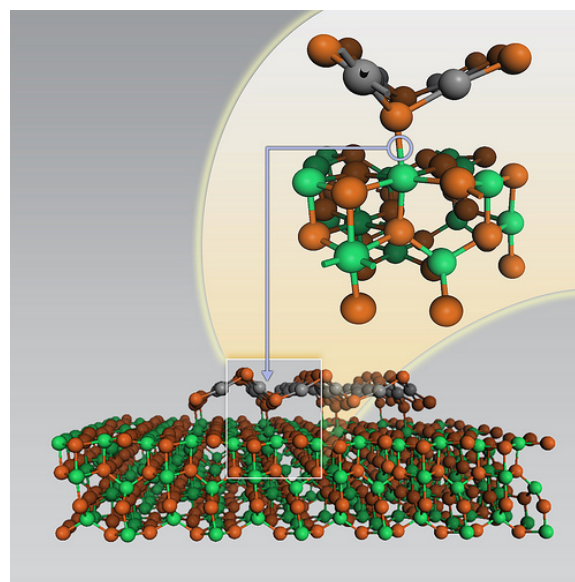


Figure 1. Rafts of catalytic platinum oxide float above a sea of aluminum oxide, anchored by bonds between platinum and aluminum.

Lastly, the team showed that penta-aluminum atoms were needed for the rafts to form. Alpha-aluminum oxide does not contain penta sites. When the researchers looked under the microscope at catalyst material formed with alpha-aluminum oxide, platinum atoms formed balls that tottered around on the surface instead of tidy rafts. Theoretical analysis that took into account all the experimental data yielded a model of how the catalyst material forms. The results provide insight into how they could produce a better performing catalyst.

Finding the conditions that will allow the chemists to control the number and distribution of penta sites will be the subject of future research. This work was supported by DOE's Basic Energy Sciences and Energy Efficiency and Renewable Energy.

Citation:

Kwak JH, J Hu, D Mei, CW Yi, DH Kim, CHF Peden, LF Allard, and J Szanyi. 2009. "Co-Ordinatively Unsaturated Al³⁺ Centers as Binding Sites for Active Catalyst Phases on γ -Al₂O₃." *Science* DOI 10.1126/science.1176745.

Observation of a Remarkable Temperature Effect in the Hydrogen Bonding Structure and Dynamics of the CN⁻(H₂O) Cluster

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Scientists have long known that molecules dance about as the temperature rises, but now researchers know the exact steps that water takes with a certain molecule. Results with small, electrically charged cyanide ions and water molecules reveal that water zips around ions to a greater extent than expected. The findings, using EMSL computational and experimental resources, improve understanding of a chemical interaction important in atmospheric sciences.

A team comprised of researchers from Washington State University, Pacific Northwest National Laboratory, Technische Universitatet Munchen, and EMSL have developed a new instrument to probe the dynamics of ions in water. Combining theory and modeling to make sense of those experiments have given the team a deeper fundamental understanding of what is happening with water. The results were published on the cover of the September 3, 2009, issue of *Journal of Physical Chemistry A*.

Atmospheric scientists want to know how small particles flutter through water vapor in the sky. To get at the basics, they study a simpler interaction: water and ions, small atoms or molecules that have a slight electrical charge and exist everywhere in nature. For example, when common table salt—sodium chloride—dissolves in water, the negatively charged chloride ions (Cl⁻) and the positively charged sodium ions (Na⁺) each interact separately with the water molecules.

Previous work with chloride ions and water has yielded conflicting results about how a water molecule (which is shaped like a boomerang) and a chloride ion (shaped like a ball) face each other. Other groups study barbell-shaped cyanide ions because many molecules found naturally in the environment contain cyanide. The chemical interactions of water and either chloride or cyanide are influenced by the charge and the shape of the molecules, as well as the temperature in which they find themselves.

But directly observing temperature's role in how water and cyanide ions interact has been difficult. So, the team developed a unique instrument that allowed them to precisely control the temperature down to almost absolute zero, or the temperature at which everything freezes. The team used temperature-controlled photoelectron spectroscopy in EMSL to determine how tightly one cyanide ion and one to three water molecules interact at the very low temperature of -438 °F (12 Kelvin) and again at ambient temperature of 80 °F (equivalent to 300 Kelvin).

The team measured the molecules' electron binding energy at low and high temperatures. This energy is an indication of how tightly the molecules hold onto their electrons—the tighter the hold, the stronger the bonds that will form between molecules. The team found that ones at low temperature exhibited higher electron binding energy than the ones at high temperatures, as they had expected. However, the difference between the two scenarios was greater than the team expected.

To explore the unexpected difference in energy, the researchers ran computer simulations on the Chinook supercomputer in EMSL. This also let them determine how the boomerang-shaped water and barbell-shaped cyanide faced each other. First they estimated how much energy the molecules used to take different configurations. Then they compared the computer-based estimates to the data they collected in their unique instrument at different temperatures. The team found that the molecules behaved differently at cold and warm temperatures. At lower temperatures, the boomerang-shaped water held still while the cyanide teetered at the end of one of water's two arms. There, the cyanide flipped, sometimes pointing its carbon (C) atom towards the water's arm, and sometimes pointing its nitrogen (N). At the coldest temperature tested, -438 °F, the molecules froze, with cyanide pointing its nitrogen end at the water.

At ambient temperatures, however, the barbell-shaped cyanide held steady while the water molecule rocked and flipped around the cyanide. Although the researchers were surprised at how much the water moved, the many positions water could take explained why they saw less electron binding energy than they expected at room temperature: A wiggly water means that the bond between molecules isn't that tight.

The results also explain the conflicting results with chloride ions and water, because of the importance of temperature on that interaction as well.

The researchers plan to follow up with studies that include many water molecules and ions at once, as well as with more complex ions than cyanide. The research was funded by DOE's Office of Basic Energy Sciences.

Citation:

Wang XB, JC Werhahn, LS Wang, K Kowalski, A Laubereau, and SS Xantheas. 2009. "Observation of a Remarkable Temperature Effect in the Hydrogen Bonding Structure and Dynamics of the CN⁻(H₂O) Cluster." *Journal of Physical Chemistry A*, DOI 10.1021/jp9034002.

Single Wall Diesel Particulate Filter (DPF) Filtration Efficiency Studies using Laboratory–Generated Particles

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Studies of how diesel particulate filters (DPFs) trap particles use a fundamental scientific approach to understand issues related to clean energy production and use. Such research has future potential to help manufacturers build better filters, a critical step toward tackling diesel exhaust emissions, leading to less air pollution.

A team of researchers from the Pacific Northwest National Laboratory used integrated computational and experimental resources at EMSL to investigate the ability of two types of diesel particulate filters—silicon carbide and cordierite—to trap small particles that diesel engines emit into our air (Figure 1). Consumers are enamored with the higher fuel efficiency diesel engines afford, but are put off by the higher exhaust particulate matter, or soot, diesel produces. Presently, DPFs are the most efficient means to trap the soot. EMSL researchers conducted a direct comparison between silicon carbide and cordierite DPFs as well as between experimental data and existing models that aim to predict DPF filtration efficiency and pressure drop. Nearly spherical laboratory-generated ammonium sulfate particles were used as soot surrogate in this study; they are ideally suited for comparing experimental results to computational simulations that treat soot agglomerates as spherical. To what extent these simplifications impact the accuracy of DPF simulations remains an open question.

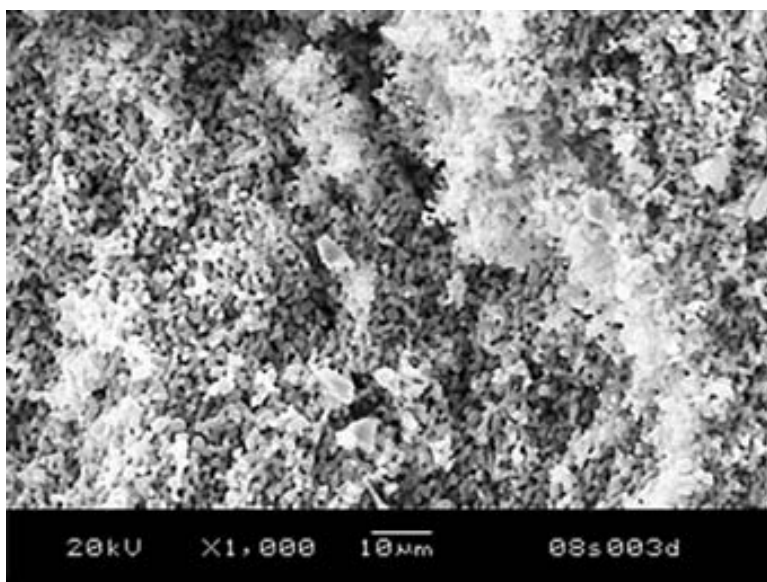


Figure 1. Scanning electron microscopy image of a single wall cordierite filter that was loaded with ammonium sulfate particles for 18 hours. The particles trapped on top of the filter form a thick cake.

The study theoretically modeled and experimentally tested the two ways in which filters block particulate matter. First, particles are captured in the filter holes; second, longer exposure causes the particles to form a dense “soot cake” on which particles are efficiently trapped. The researchers showed that the transition from filter capture “soot cake” can be identified by recording the change in pressure across the filters as a function of particle loading and that the filters trap small and large particles better than particles that are ~80 to 200 nm in aerodynamic diameter. Comparing experimental data and a simulation showed that the models overpredict the filter’s trapping efficiency, and as a result they also predict shallower penetration than that observed in the experiment. The team will travel to Wisconsin to collaborate with General Motors and the

University of Wisconsin researchers to investigate the behavior of DPFs when exposed to laboratory-generated soot particles and particles emitted by diesel engines under various operating conditions. The collaborators plan to characterize the physical and chemical properties of particle matters using EMSL's Single-Particle Laser Ablation Mass Spectrometer, or SPLAT II.

This work, supported by the DOE Office of Energy Efficiency and Renewable Energy, was featured in *Chemical Engineering Science*.

Citation:

Yang J, M Stewart, GD Maupin, DR Herling, and A Zelenyuk. 2009. "Single wall diesel particulate filter (DPF) filtration efficiency studies using laboratory-generated particles." *Chemical Engineering Science* 64(8):1625-1634.

No Confinement Needed: Observation of a Metastable Hydrophobic Wetting Two-Layer Ice on Graphene

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(b) Ruhr-Universität Bochum, Bochum, Germany

For the first time, scientists have built completely flat, two-layer ice. While theoreticians have predicted that such ices are formed by squeezing water molecules between two surfaces, EMSL users from Pacific Northwest National Laboratory and Ruhr-Universität Bochum are the first to create it. All it took was collaboration, creativity, and the absence of pressure. Creating this type of ice shows the structure of water on a water-fearing, or hydrophobic, surface. The structure of water at these surfaces is vital to understanding protein folding, and the assembly of cellular membranes and intracellular compartments.

Close collaboration between theoreticians and experimentalists from Pacific Northwest National Laboratory and Ruhr-Universität Bochum, along with well-equipped laboratories and a supercomputer, allowed the team to build a layer of ice two molecules thick and then to determine how the atoms and electrons in that ice arranged themselves.

The experimentalists began with a thin sheet of carbon, known as graphene on top of a layer of platinum. Then, they introduced a small amount of water onto the surface in ultrahigh vacuum (that is, no pressure) and very low temperatures. While ice traditionally forms at 273 Kelvin, for this experiment, the temperature was dropped to 125 K, about the temperature of an evening on the moon.

Next, the team used low-energy diffraction equipment that sends waves of slow-moving electrons at the surface. How those electrons bounce off the surface tells researchers a lot about the structure of the material.

The researchers found a layer of smooth ice had grown on the graphene, not the usual puckered layers of ice seen on water friendly or hydrophilic surfaces. In the new ice, the angles between the atoms in the water molecules were stretched or compressed compared to normal ice. So, the team subjected the ice to infrared spectroscopy, giving them information on how the water molecules were vibrating in the ice film. These results confirmed that the water molecules were in unusual configurations.

With these results, the theoreticians did complex calculations that determined the position of each of the atoms in the ice layer. The calculations were done with the software NW-ICE on a supercomputer at EMSL (Figure 1). The theoreticians found that in each layer of the ice, the water molecules formed slightly larger rings than normal. These six-sided rings stacked on top of each other, when looking down through the layers. They also found that each water molecule formed four hydrogen bonds—three with other molecules in the same layer, and one with water in the other layer. They also found that there are two types of water molecules: One type is parallel to the surfaces of the ice and its H-O-H angle is larger than normal. The other type connects the two layers and its H-O-H angle is smaller than normal.

The team, again integrating experiments and theory, are studying the temperature range over which the two-layer ice is stable and what happens when more water is added on top of the two-layer ice.

The research was supported by DOE's Office of Basic Energy Sciences and partially by Deutsche Forschungsgemeinschaft and by Fonds der Chemischen Industrie. The research was featured in *Journal of the American Chemical Society*.

Citation:

Kimmel GA, J Matthiesen, M Baer, CJ Mundy, NG Petrick, RS Smith, Z Dohnalek, and BD Kay. 2009. "No Confinement Needed: Observation of a Metastable Hydrophobic Wetting Two-Layer Ice on Graphene." *Journal of the American Chemical Society* 131(35):12838.

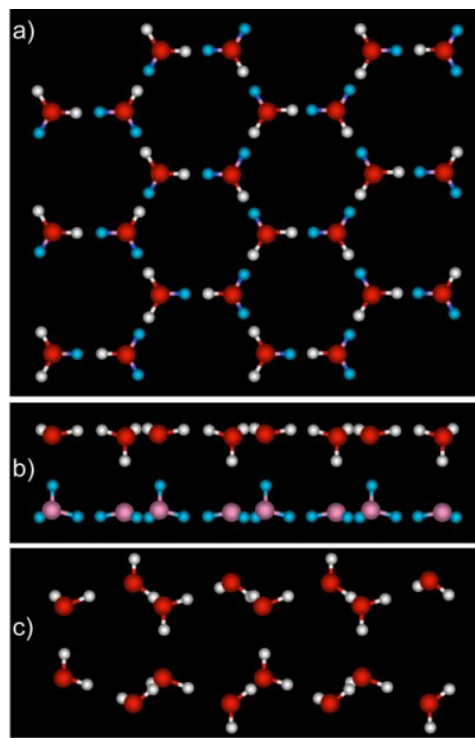


Figure 1. (a) Top view. The two-layer ice has hexagonal symmetry. (b) Side view. Two flat layers of molecules with hydrogen bonds connecting the layers. (c) Side view of normal, puckered hexagonal ice.

Defect-Enhanced Charge Transfer by Ion-Solid Interactions in SiC using Large-Scale *Ab Initio* Molecular Dynamics Simulations

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(b) University of Electron Science and Technology of China, Chengdu, China

(c) Forschungszentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, Dresden, Germany

Radiation can come in a seemingly benign form like sunlight or in a more destructive form to materials, as in nuclear reactors and outer space. Either way, radiation interacts with the materials it touches. Understanding how those interactions damage or affect the properties of the material has challenged traditional computer modeling and simulation approaches. Now a team of EMSL users has shown that how electrons respond to radiation in a solid can alter the way permanent damage is created in the material

and radically affect its mechanical, magnetic, electrical, and optical properties. Understanding how defects are formed helps researchers understand how material is changed by radiation, which is important for safe nuclear power and space exploration

Hard materials such as the steel used in nuclear reactors or natural minerals such as diamond look stable, but radiation exposure kicks the material's atoms off their highly organized lattices as ions that move freely inside the lattice. Previous studies led scientists to believe that the ions smashed into each other like cars in a demolition derby, with each ion car being a hard particle with immovable electrons embedded in the car's surface.

The team of EMSL users from Pacific Northwest National Laboratory, University of Electron Science and Technology of China, and Forschungszentrum Dresden-Rossendorf is finding that simply isn't the case. Instead of being embedded in the ion cars, the electrons sit like a cloud of exhaust around each ion, and they can actually leap from ion to ion and back again. The way they leap affects how the ions react to each other. Ions may move farther apart or closer, speed up or slow down. The researchers need to understand at a fundamental level how energy is transported by both electrons and ions. They used much higher-level theoretical calculations to look deeper than the level of the atom to understand the response and role of the electrons.

In a relatively new approach, the scientists used a single blast of low-level radiation to create damage, or atomic defects, in a silicon-based material so they could study the movement of both the electrons and silicon ions. Using supercomputers at EMSL and the National Energy Research Supercomputing Center, the researchers found that electrons jumped back and forth from the moving silicon ion to surrounding atoms (Figure 1). This movement ultimately created permanent defects, or damage, in the material. The researchers also found that electrons can be trapped by the defects created.

The work is the first time such intensive calculations could be performed. The team modified state-of-the-art software and took advantage of recent advances in computer hardware to perform the calculations. They now hope to apply the work to more complex materials to look at how trapped electrons affect the way defects move and interact with each other when the material is exposed to more than one blast of radiation over longer times in much larger systems and at higher levels of radiation. Improved understanding and modeling of how electrons and ions respond to radiation will lead to improved materials and performance in safely managing nuclear fuels and waste forms.

This work was supported by the DOE Office of Basic Energy Sciences; the Department of Applied Physics, University of Electronic Science and Technology of China; and the Forschungszentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research in Dresden, Germany.

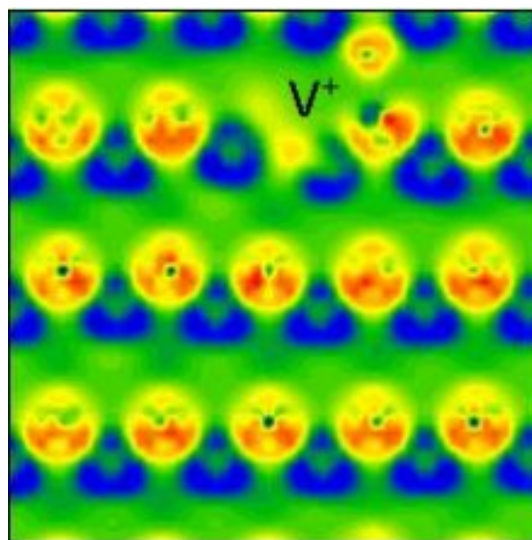


Figure 1. Scientists were surprised to find that electrons jump between ions when material is exposed to low levels of radiation, and how the charged vacancy, shown in yellow and indicated by V^+ , is formed.

Citation:

Gao F, H Xiao, X Zu, M Posselt, and WJ Weber. July 2009. "Defect-Enhanced Charge Transfer by Ion-Solid Interactions in SiC using Large-Scale *Ab Initio* Molecular Dynamics Simulations." *Physical Review Letters* 103(2):02745. DOI: 10.1103/PhysRevLett.103.027405

On the Phase Diagram of Water with Density Functional Theory Potentials: The Melting Temperature of Ice I_h with the Perdew–Burke–Ernzerhof and Becke–Lee–Yang–Parr Functionals

S Yoo,^(a) XC Zeng,^(b) and SS Xantheas^(a)

(a) Pacific Northwest National Laboratory, Richland, Washington

(b) University of Nebraska, Lincoln, Nebraska

Two popular computer models used by chemists and physicists to describe water do not correctly predict that ice melts at 32 degrees Fahrenheit, according to a study by EMSL users from Pacific Northwest National Laboratory and the University of Nebraska, Lincoln, that was compiled with the help of EMSL computing resources. More important, the study suggests that simulations of liquid water at room temperature with those models actually describe a supercooled glassy state, not the regular liquid. The study in the May 2009 Journal of Chemical Physics was the #3 download paper in June.

The team pointed out the problem in two of the most popular DFT, or density functional theory, models in predicting the correct phase diagram of water. A DFT model describes the underlying interactions between water at the molecular level, incorporating the interactions between the nuclei and the electrons of the system. Both of those DFT models suggest that the melting temperature of ice is way too high, almost 150°F higher than the value that nature has settled on. So if you use those models to describe water at room temperature, you do not get the regular liquid but instead a supercooled glassy state that does not look like nature's most ubiquitous solvents. This finding will help researchers fine tune DFT models to achieve a closer match to what's observed during experiments.

Whether studying clouds, cancer, or catalysts, the behavior of water is the key factor. Clouds form from water and act as a testbed for a variety of processes that ultimately affect earth's climate. Cancer treatments must work with the water found in cells. And catalysts both speed reactions in water and use the liquid as a feedstock to create renewable energy sources such as hydrogen.

Scientists in all of these fields need to understand, at the molecular level, how water behaves under different conditions and in different environments. For example, how does the behavior of water molecules and sulfur oxide impact the creation of acid rain? The DFT models are used to understand how changes at the atomic and molecular levels influence behaviors we can see and touch. The more realistic these models are, the easier time scientists have understanding and controlling reactions.

The research, which was supported by DOE's Office of Basic Energy Sciences and the Nebraska Research Initiative, was featured in *Journal of Chemical Physics*.

Citation:

Yoo S, XC Zeng, and SS Xantheas. 2009. "On the Phase Diagram of Water with Density Functional Theory Potentials: The Melting Temperature of Ice I_b with the Perdew-Burke-Ernzerhof and Becke-Lee-Yang-Parr Functionals." *Journal of Chemical Physics* 130:221102.

***In Situ* Studies of Soft- and Reactive Landing of Mass-Selected Ions Using Infrared Reflection Absorption Spectroscopy**

Q Hu,^(a) P Wang,^(a) PL Gassman,^(a) and J Laskin^(a)

(a) Pacific Northwest National Laboratory, Richland, Washington

For the first time, researchers can determine if large molecules and other charged particles that softly land on a surface form the desired bonds, thanks to a new approach built by a team of EMSL users at Pacific Northwest National Laboratory. This method, developed using EMSL capabilities, relies on in situ reflection-absorption spectroscopy to monitor the formation of a chemical bond between the ion and the surface. In designing specialized sensors and other technologies, scientists want to prepare customized layers of molecules on specific surfaces. To build these layered materials, scientists must first understand the reactions involved. This new tool provides vital insights on the reactivity between ions and surfaces. Using it, scientists can study bond formation and the impact of the surface on the secondary structure and orientation of large molecules that land on it.

Using this new approach (Figure 1), the team made a startling discovery about the efficiency of bond formation between the ion and the surface. Using diamine, a linear molecule with nitrogen atoms at each end, as a model ion, they found that nearly every ion that hit the surface bonded to it—a very surprising result.

To study bond formation between ions and reactive surfaces, researchers previously had to expose surfaces to a beam of mass selected ions, then take the substrate outside the vacuum system and perform the analysis. But, as a general rule, researchers prefer to study reactions as they happen as exposure of surfaces to laboratory air can alter the structure of deposited molecules and introduce artifacts.

The researchers selected for their experiments a long chain-like molecule, with 12 carbon atoms in the middle and an amine group on each end. Ions of this molecule were selected using a mass filter and were sent to react with a carbon-based surface by forming an amide bond. This bond involves a carbonyl group (C=O) on the substrate and an amine group (NH₂) of the ion each shedding off other atoms and bonding together. Surprisingly, the researchers found that nearly every molecule that hit the surface bonded. In the past, studying bond formation between small proteins or peptides and surfaces using infrared spectrometry was difficult because the signals indicating the formation of a new amide bond between the surface and the protein were buried under strong infrared bands of the protein itself. Now, scientists can study the reactions as they occur. The new approach allows researchers to unambiguously prove that bond formation indeed takes place and quantify the amount of amide bonds formed.

However, initial bond formation just one part of a bigger picture. Researchers can also study how the surface affects the material that land on it. For example, placing a large molecule that is happy in water on a surface that repels water will cause the molecule to reorganize. Because the conformation of a large molecules

determines its function, understanding this phenomenon is essential for designing nanomaterials with controlled properties. This new technique will help answer questions about how such rearrangements occur.

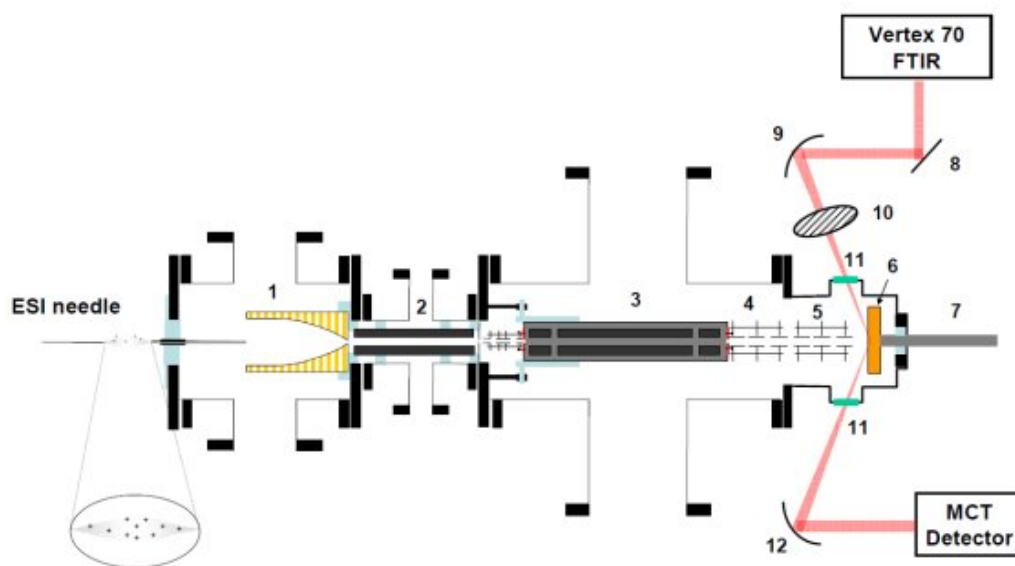


Figure 1. Scientists can now determine if ions form the desired bonds to a surface, thanks to a modified ion soft landing instrument. The schematic shows (1) ion funnel, (2) collisional quadrupole, (3) mass filter, (4) and (5) two lenses, (6) surface, (7) linear motion feedthrough for positioning of the surface, (8) flat mirror, (9) and (12) parabolic mirrors, (10) MIR wire grid polarizer, (11) viewports.

In the future studies, the scientists will examine the effect of the substrate on the orientation and conformation of soft-landed peptides and proteins. In addition, they are continuing their work to understand the interactions between molecules and surfaces to arrive at the time when understanding leads to controlled preparation of functional materials. Further, with this new method available at EMSL, scientists from around the world have another tool in their arsenal to study bond formation. Already, a scientist from the University of Arizona, through EMSL's rapid access program, is using the approach for his studies.

This research, funded by DOE's Office of Basic Energy Sciences, was featured in *Analytical Chemistry*.

Citation:

Hu Q, P Wang, PL Gassman, and J Laskin. 2009. "In Situ Studies of Soft- and Reactive Landing of Mass-Selected Ions Using Infrared Reflection Absorption Spectroscopy." *Analytical Chemistry* 81:7302-7308. DOI: 10.1021/ac901149s.

An Isotropic Chemical Shift–Chemical Shift Anisotropic Correlation Experiment using Discrete Magic Angle Turning

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(a) Pacific Northwest National Laboratory, Richland, Washington

(b) EMSL, Richland, Washington

A new nuclear magnetic resonance capability developed at EMSL—called DMAT—will allow researchers to gain new insights into catalytic reactions, which may lead to an improved ability to tailor catalysts for optimal performance for applications such as alternative energy production and environmental remediation. In addition, DMAT can be used to collect novel data for—and, therefore foster a stronger fundamental understanding of—biological systems, such as dense cell systems and cells attached to solid surfaces.

The DMAT (Figure 1), or discrete magic angle turning, apparatus and method was developed by researchers at the Pacific Northwest National Laboratory's Institute for Interfacial Catalysis and EMSL, and merited a United States patent.

DMAT combines the advantages of two established NMR technologies: magic angle hopping and magic angle turning. MAH and MAT are built from the cornerstone of NMR, magic angle spinning, which produces high-resolution, high-sensitivity isotropic spectra. But traditional MAS at a sample spinning rate of several kHz cannot be adapted for *in situ* investigations that require simultaneous, elevated pressure and flow controls. MAH allows simultaneous control over sample conditions (pressure, flow, and temperature) and generates enhanced structural data, but technical difficulties limit its wide-spread application for *in situ* experiments. MAT overcomes some of the technological challenges of MAH, but cannot be applied to *in situ* investigations that require precise pressure control. DMAT combines the best of both worlds of MAH and MAT and showed great potential in preliminary experiments. For example, DMAT structural data on 1,2,3-trimethoxybenzene were significantly enhanced compared to MAH and similar to that obtained with MAT, and this data quality was coupled with the ability to control sample temperature, pressure, flow conditions, and reactant feed composition *in situ* and simultaneously.

The simultaneous *in situ* control over sample conditions afforded by DMAT will open new doors for researchers to conduct *in situ* NMR studies of catalytic reactions and biological systems. The invention garnered a U.S. patent, *Discrete Magic Angle Turning System, Apparatus, and Process for in situ Magnetic Resonance Spectroscopy and Imaging*, Patent Number US 7,535,224 B2, and supports EMSL's goals to characterize surfaces and interfaces with unprecedented resolution as well as to predict biological functions from molecular and chemical data.

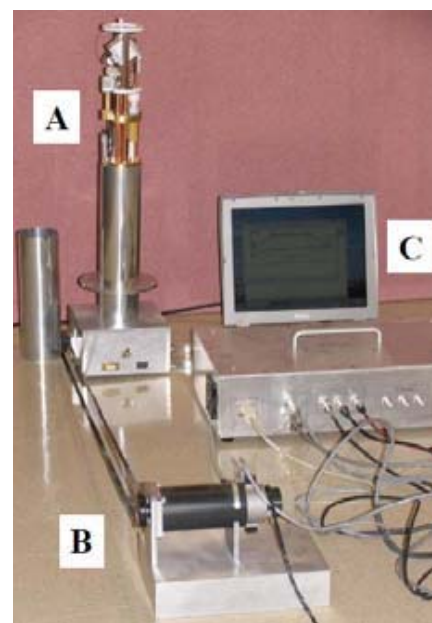


Figure 1. The DMAT apparatus consists of three parts: a specialized NMR probe (A), a DC Servo motor (B), and a computer-programmed box that precisely controls the rotation of the motor (C).

This work was supported by the DOE Office of Basic Energy Sciences and by EMSL's Intramural Research Program. It was featured in *Journal of Magnetic Resonance*.

Citation:

Hu JZ, JA Sears, JH Kwak, DW Hoyt, Y Wang, CHF Peden. 2009. "An Isotropic Chemical Shift-Chemical Shift Anisotropic Correlation Experiment using Discrete Magic Angle Turning." *Journal of Magnetic Resonance* 198:105–110.

Defining the Active Catalyst Structure and Reaction Pathways from *Ab initio* Molecular Dynamics and *Operando* XAFS: Dehydrogenation of Dimethylaminoborane by Rhodium Clusters

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(b) EMSL, Richland, Washington

To use hydrogen as a clean energy source, some engineers want to pack hydrogen into a larger molecule, rather than compressing the gas into a tank. A gas flows easily out of a tank, but getting hydrogen out of a molecule requires a catalyst. Now, researchers reveal new details about one such catalyst. The results are a step toward designing catalysts for use in hydrogen energy applications such as fuel cells.

EMSL researchers and users Pacific Northwest National Laboratory combined experimental and theoretical studies to identify the characteristics of the catalyst, a cluster of rhodium, boron and other atoms. The catalyst chemically reacts with ammonia borane, a molecule that stores hydrogen densely, to release the hydrogen as a gas (Figure 1). Their results, which reveal many molecular details of this catalytic reaction, was featured in *Journal of the American Chemical Society*.

Researchers and engineers are trying to create a hydrogen fuel system that stores hydrogen safely and discharges hydrogen easily, which can then be used in fuel cells or other applications. One way to achieve such a fuel system is by "storing" hydrogen as part of a larger molecule. The molecule that contains hydrogen atoms, in this case ammonia borane, serves as a sort of structural support. The catalyst plucks the hydrogen from the ammonia borane as needed to run the device.

The researchers study a rhodium-based catalyst that performs this job fairly well, but might have potential for improvement. Their initial work showed that the catalyst worked as a molecule that contained a core of four rhodium atoms in a tetrahedron, or a triangular pyramid, with each corner decorated with boron and other elements. But the rhodium and other atoms could line up in dozens of configurations in the molecule. That wasn't enough information for design improvements - the team wanted to know which of the multitude of structures was the real catalyst, as well as how the atoms worked together to remove the hydrogen from ammonia borane. To find out, the researchers had to combine experimental work with theoretical work, because neither method was sufficient on its own.

First, the team followed the catalyst-ammonia borane reaction with several technologies. One of the most important is an uncommon technique known as *operando* XAFS, which allowed them to take X-ray snapshots of the catalyst in action. Most researchers examine a catalyst's structure when the catalyst is at a standstill, but that is like trying to figure out how an athlete performs by watching him sleep. Additional experiments were performed in EMSL. The data from the various experiments were like puzzle pieces that the team had to fit together.

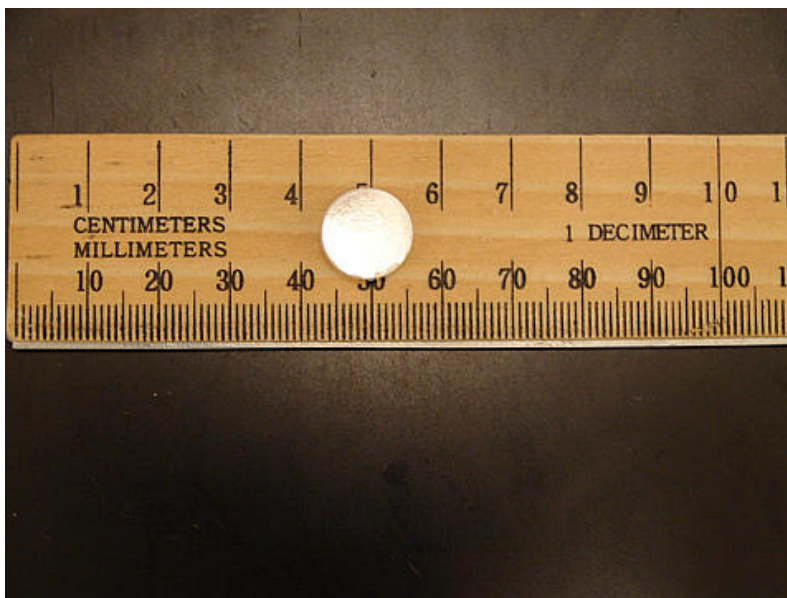


Figure 1. A small pellet of solid ammonia borane (240 mg), as shown, is capable of storing relatively large quantities of hydrogen (0.5 liter) in a very small volume.

To put the puzzle together, the team used computer models to construct a theoretical molecular configuration that accounted for all the data. These computationally challenging models were calculated on computers at the National Energy Research Scientific Computing Center at Lawrence Berkeley National Laboratory in Berkeley, California. The computer model produced a structure that best incorporated the experimental data. To test whether this structure worked properly, the team performed a computer simulation of an *operando* XAFS analysis of that catalytic structure reacting with ammonia borane. Then they compared the simulated data with real data gathered about the catalyst. The two sets of data matched very well, suggesting the structure they had come up with was very close to reality.

The chemical nature of the structure, along with additional experimental data, allowed the team to outline the chemical reaction occurring between the catalyst and the ammonia borane. The catalyst does not remain still, making it a good catalyst but, like an active two-year old, also a difficult subject to pin down.

The results suggested that the active catalyst picks off hydrogen from a particular spot on the ammonia borane molecule: a nitrogen atom in the molecule holding onto two hydrogen atoms. First, the catalyst plucks one hydrogen atom off. This is the hardest part of the reaction and it makes the bond between the remaining hydrogen and boron unstable. So the molecule spits off the second hydrogen as well, and the two hydrogen atoms form molecular hydrogen, or H₂ which is released as a gas and can be used in engines or fuel cells.

Additional details remain to be drawn out by the team, but this study makes a big dent in what they need to know to design a good, inexpensive catalyst.

This work was supported by DOE's Basic Energy Sciences Program and was featured in the *Journal of the American Chemical Society*.

Citation:

Rousseau R, GK Schenter, JL Fulton, JC Linehan, MH Engelhard, and T Autrey. 2009. "Defining the Active Catalyst Structure and Reaction Pathways from *Ab initio* Molecular Dynamics and *Operando* XAFS: Dehydrogenation of Dimethylaminoborane by Rhodium Clusters." *Journal of the American Chemical Society* DOI 10.1021/ja901480u.

Low-Energy Networks of the T-Cage (H₂O)₂₄ Cluster and Their Use in Constructing Periodic Unit Cells of the Structure I (sI) Hydrate Lattice

S Yoo,^(a) MV Kirov,^(b) and SS Xantheas^(a)

(a) Pacific Northwest National Laboratory, Richland, Washington

(b) Siberian Branch of the Russian Academy of Sciences, Tyumen, Russia

There's a lot more to water than meets the eye. Water molecules form three-dimensional empty cages organized in a lattice with the potential to store large amounts of natural gases. Gases such as hydrogen, methane, and carbon dioxide can be fit as "guest" molecules inside these "host" cavities. But water molecules can be arranged in millions of ways in the basic unit cell, and scientists need to know those arrangements that are energetically more stable compared to others, because lower-energy, stable arrangements have the greatest potential for storing energy. With millions of possible combinations, finding the ones that are lower in energy becomes a challenge of staggering proportions. Now a computer model built by EMSL users from the Pacific Northwest National Laboratory and the Russian Academy of Sciences allows scientists to rapidly pinpoint the most stable structures and use them to model those systems that hold promise for energy storage (Figure 1).

At high pressures and low temperatures, like those found in permafrost or on the ocean's floor, water molecules organize into complex hydrate lattices that are held together by hydrogen bonds. Because these lattices are so complex, even sophisticated computer models struggle to find the lattices of most interest to researchers.

Previous methods used to analyze lattices relied on a "top down" approach. Under those methods, researchers started with the known arrangement of the oxygen atoms and randomly selected the positions for the hydrogen atoms to build a network that obeyed certain rules. That approach had several drawbacks. It was based on statistical sampling, which required very large unit cells to be effective. Then too, the resulting structures could be more theoretical than practical, meaning they might not exist in reality. Even more problematic, the model couldn't guarantee that the most appropriate structures would even be found.

The new approach starts from the bottom, by looking at the building blocks of the hydrate lattices and the characteristics needed for stability. Researchers then use these blocks to build the more complex lattices. This approach ensures that the resulting structures meet all requirements for stability.

The computer model screens quickly through all possible configurations of the water cages that are used to build the hydrate lattice by calculating the energy necessary to hold each collection of water molecules

together. Some arrangements require very large amounts of energy to make. These are discarded. Others need less energy to build. These are most likely the arrangements that would actually exist.

PNNL chemist Dr. Sotiris S. Xantheas and colleagues Dr. Soohaeng Yoo, also at PNNL, and Dr. Mikhail Kirov of the Russian Academy of Sciences had previously applied this approach on a smaller arrangement consisting of a hollow cage of 20 water molecules. They narrowed an initial list of 30,026 possible arrangements down to 64, which were most likely to be the more stable ones. The most recent calculations involved hollow cages of 24 water molecules. The model refined the list of over three million structures down to just 321. With the use of the supercomputer at EMSL, the team performed detailed electronic structure calculations to further refine those arrangements. The researchers were then able to computationally build up the unit cells into a three-dimensional structure I (sI) hydrate lattice that is capable of holding the alternative energy source hydrogen as well as natural gases.

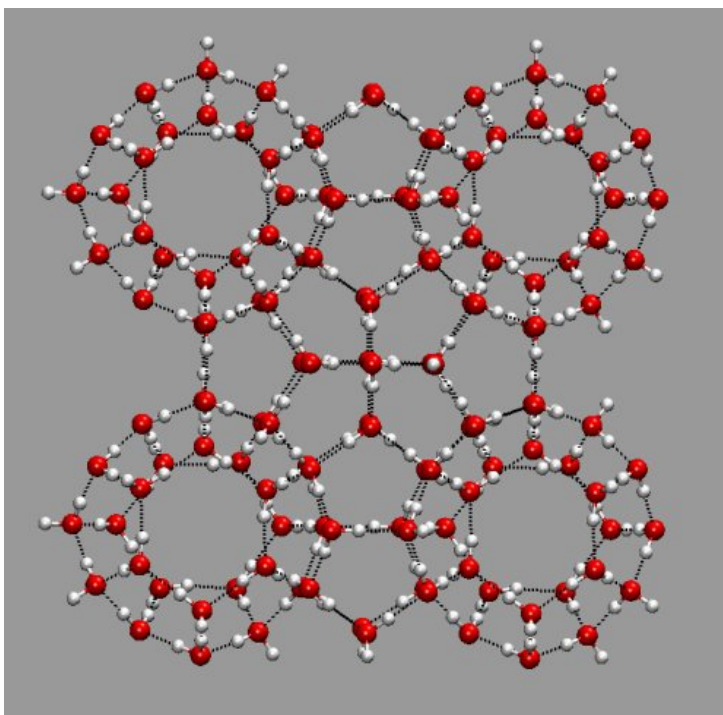


Figure 1. Researchers use an innovative model to identify the most stable water molecule lattices for energy storage.

The work provides realistic models for the hydrate lattices and allows researchers to understand the underlying intermolecular interactions that are responsible for storing "guest" molecules in these "host" lattices.

Water molecules form hydrate lattices in three types of structures, labeled sI, sII, and sH. The current work modeled the sI hydrate lattice. In the future, the researchers hope to model the sII hydrate lattice, for which the unit cell is made from 16 units of hollow cages with 20 water molecules each and 8 units of an even larger hollow cage of 28 water molecules that can have over 60 million possible arrangements. The (sII) hydrate has been reported to meet current Department of Energy's target densities for an on-board hydrogen storage system.

DOE's Office of Basic Energy Sciences and the Russian Academy of Sciences funded the research, which was featured in the *Journal of the American Chemical Society*.

Citation:

Yoo S, MV Kirov, and S Xantheas. "Low-Energy Networks of the T-Cage (H₂O)₂₄ Cluster and Their Use in Constructing Periodic Unit Cells of the Structure I (sI) Hydrate Lattice." Communication to the Editor, *Journal of the American Chemical Society* 131(22):7564-7566.

Awards and Recognition

Campbell testifies before House Committee. Allison A. Campbell, Director of EMSL, testified on September 10, 2009, before the Subcommittee on Energy and Environment of the House Committee on Science and Technology about how EMSL's unique facilities and instruments help DOE meet its mission goals through biological research. See the PNNL news release and video at <http://www.pnl.gov/news/release.aspx?id=400>.



Allison Campbell



Nathan Yee

Yee garners geochemistry honors.

Geochemistry research by EMSL user **Nathan Yee** (Rutgers University) has garnered two honors this year. First, it was selected and cited in July 2009 in *Science* as an Editor's Choice in the area of Geochemistry. Also, his research earned him the 2009 Houtermans' medal from the European Association for Geochemistry. Using sophisticated instruments, including electron and Mössbauer spectrometry at the Department of Energy's EMSL, Yee leads studies on how microbes reduce or mediate the toxicity of mercury and other metals. These studies are providing information to aid in designing effective contaminant sequestration technologies, key to halting toxins movement toward rivers and other waterways. The Houterman medal honors a young researcher, no more than

35 years of age, who has made exceptional contributions to geochemistry. Yee received this honor at the Goldschmidt Conference in Davos, Switzerland.

Kukkadapu recognized as international leader in Mossbauer spectroscopy. EMSL researcher **Ravi Kukkadapu** recently received two international honors in the Mössbauer spectroscopy community. At the International Conference on the Applications of the Mössbauer Effect in Vienna, Austria, he was featured as an emerging leader in the Mössbauer community. He received this honor from distinguished Professor John Stevens, Director of the Mossbauer Effect Data Center, a research institute at the University of North Carolina. In addition, Kukkadapu was invited to give a keynote talk at the upcoming Clay Minerals Group of the Mineralogical Society in the United Kingdom. At this annual conference, he will discuss the effect of iron-mineral (bio)transformations on remediating contaminated aquifers that contain radioactive metals such uranium, technetium, and plutonium. Contaminated aquifers, which can occur during nuclear material production and weapons development, are a problem worldwide.



Ravi Kukkadapu

Tartakovsky earns PECASE Award. EMSL user **Alexandre Tartakovsky**, a computational mathematician from Pacific Northwest National Laboratory, has been recognized with a Presidential Early Career Award for Scientists and Engineers. The award honors his research on subsurface flow that addresses past and future energy needs: cleaning up buried nuclear or toxic contaminants and storing carbon dioxide from fossil fuels underground. Announced by the White House, the PECASE is the highest honor given by the U.S. government to scientists and engineers who are at the start of their careers. Tartakovsky earned



Alexandre Tartakovsky

this award for his work trying to understand how contaminants move through the subsurface, that subterranean environment made of rocks, air, liquids like water or oil, and bacteria. Ultimately, such work will help reduce the impacts that nuclear and fossil fuel energy use have on the environment. Tartakovsky develops mathematical models to help researchers clean up nuclear or toxic contaminants from past practices or help future waste managers store carbon in the subsurface.



Jean Futrell

Futrell elected Fellow of ACS. Former EMSL Director **Jean Futrell** was selected for the inaugural class of American Chemical Society Fellows. The American Chemical Society, with more than 150,000 members, is one of the world's largest scientific organizations. This prominent honor, given to only 0.1% of the society's members, reflects Futrell's scientific achievements and his contributions to the research community. His research focuses on the theory and practice of mass spectroscopy. His work has answered fundamental questions about mass spectrometry, including the behavior of ions. He has developed or modified instruments for specialized research, creating high-pressure and chemical-ionization mass spectrometers. His invention of tandem mass spectrometry is deployed in nearly every commercial mass spectrometer.

Koppenaar elected division chair for American Chemical Society.

David Koppenaar, Chief Technology Officer at EMSL, has been elected to a national society-level position for the American Chemical Society. He will serve as Chair-Elect for the Analytical Chemistry Division of the society starting October 1, 2009, and succeed to Program Chair in 2010 and Chair in 2011. The Analytical Chemistry Division is one of the largest of 34 divisions of the ACS, the world's largest scientific society. The division has approximately 9500 members, and its vision is "Improving people's lives through the transforming power of analytical chemistry and promoting the community of analytical scientists."



David Koppenaar



Daniel López-Ferrer

López-Ferrer receives 2008 M.T. Thomas Award. Daniel López-Ferrer, a postdoctoral fellow in the Pacific Northwest National Laboratory's Biological Separations and Mass Spectrometry Group, was selected as the 2008 recipient of EMSL's M.T. Thomas Award for Outstanding Postdoctoral Achievement. This award acknowledges outstanding accomplishments by postdoctoral fellows who have conducted their research at EMSL during the past year. It is named in honor of Dr. M. Tom Thomas, a former PNNL staff member who played an integral role in the conceptualization of EMSL.

Dr. López-Ferrer was chosen for his remarkable contributions to high-throughput proteomics. He developed and characterized a high-pressure enzymatic digestion system that can be fully integrated in an on-line process. His discovery, aided by EMSL's unmatched mass spectrometry capabilities, is opening a new realm of research possibilities for EMSL users. The methodologies he developed for processing complex biological samples have been successfully demonstrated among other EMSL projects and documented in several journal publications.

The high-pressure enzymatic digestion system developed by Dr. López-Ferrer and his colleagues in EMSL was licensed by Pressure Biosciences, Inc., a company that provides technology to control biomolecular interactions. A patent is pending, and PNNL has submitted this technology for a 2009 R&D 100 Award. According to Battelle Fellow Dr. Richard D. Smith, who nominated Dr. López-Ferrer for the award, Daniel "has been the creative force behind a number of technical advances that benefit EMSL's high-throughput proteomics capability by overcoming the bottleneck in throughput at the front end of the workflow."

Dr. López-Ferrer received his Ph.D in Biochemistry from the Autonomous University of Madrid, Madrid, Spain, in 2006. He has been a PNNL postdoctoral research associate since 2006.

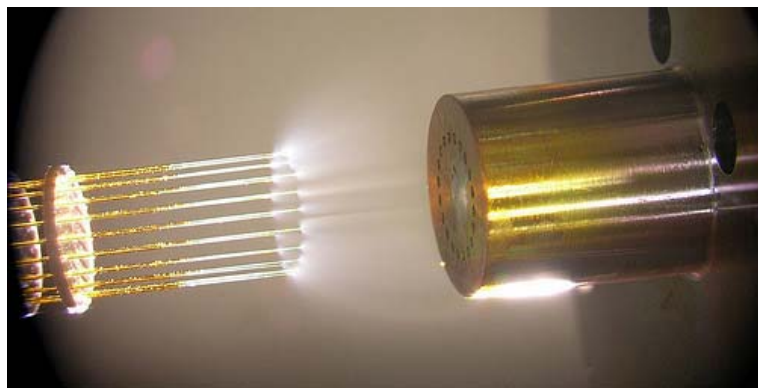


Figure 1. The Ultrasensitive ESI-MS Source and Interface developed at EMSL provides at least a 40-fold increase in mass spectrometry sensitivity relative to commercially available instruments. This ultrasensitive instrument can aid in biological and environmental studies, among others.

Integrating resources at EMSL helps scientists win R&D 100 Award. When characterizing small, hard-to-acquire samples, scientists need sensitive instruments that can provide highly accurate data. By integrating a combination of inventions and approaches at EMSL, scientists achieved at least a 40-fold increase in the sensitivity of mass spectrometers and earned an R&D 100 Award for their efforts. Known as the Oscars of the research world, R&D magazine presents the awards annually to the 100 most innovative scientific and technical breakthroughs of the year. The Ultrasensitive Electrospray Ionization-Mass Spectrometry (ESI-MS) Source &

Interface was developed by EMSL users **Dick Smith, Ryan Kelly, Jason Page, and Keqi Tang** of Pacific Northwest National Laboratory. The ESI-MS can measure amounts of compounds in a sample very precisely, even when very little material is available. This sensitivity is especially important when sample sizes are limited, such as from microbiopsies of human tissue or proteins extracted from small sediment samples. Scientists at PNNL are using the improved sensitivity in fundamental biological and environmental studies, to develop biomarkers for early disease diagnosis, and to discover drug targets. Further, they are collaborating with a major vendor of mass spectrometry instruments to further explore the benefits of the new ESI-MS system.

Chambers and Cho named Wiley Research Fellows. EMSL users **Scott Chambers** and **Herman Cho** (Pacific Northwest National Laboratory) are the first Wiley Research Fellows. The program recognizes scientists who make significant contributions to EMSL outside of their individual research efforts. As Fellows, Chambers and Cho will contribute to EMSL decision-making processes, including serving on advisory committees and participating on new capability proposals. In recognition of their work, they can request time on high-demand instruments normally reserved for EMSL staff.

Chambers was selected for his scientific and technological leadership in growing well-defined oxide films and surfaces. Such materials are of interest in photocatalysis, surface geochemistry, and other scientific areas. As a thin films expert, Chambers spends time assisting EMSL users with designing experiments and preparing samples. As a Wiley Research Fellow, he will lead the design and construction of EMSL's third generation oxygen plasma assisted molecular beam epitaxy system. The system will enable growing oxide films of increasing complexity. Chambers is a Laboratory Fellow at Pacific Northwest National Laboratory.

Cho was chosen for his leadership in developing EMSL's radiological nuclear magnetic resonance (NMR) capabilities. These capabilities are



Scott Chambers



Herman Cho

critical in studies such as radioactive waste storage forms and radionuclide migration in the subsurface. As a Wiley Research Fellow, he will provide advice and support to the design and construction of EMSL's radiological annex. The annex will provide specialized instruments, including NMR spectroscopy, for the characterization and analysis of radiological materials. Cho is a senior research scientist at PNNL. The Fellows program is named after William R. Wiley. A Laboratory Director at PNNL, he helped take EMSL from an idea to a world-class facility. Wiley felt that EMSL would help the world respond to scientific challenges that depended on fundamental science.

Visitors and Users

Year to date in Fiscal Year 2009, a total of 734 users benefited from EMSL capabilities and expertise. This total included 490 onsite users and 244 remote users.

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Book Section

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Wang, XB, and LS Wang. 2009, "Photoelectron Spectroscopy of Multiply Charged Anions." in *Annual Review of Physical Chemistry*, Vol 60, pp. 105-26. Annual Reviews, Inc., Palo Alto, CA.

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