

**EMSL Report**  
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## Research Highlights

### Determination of Phosphorus Speciation by Solid-State $^{31}\text{P}$ NMR Spectroscopy: Environmental Applications

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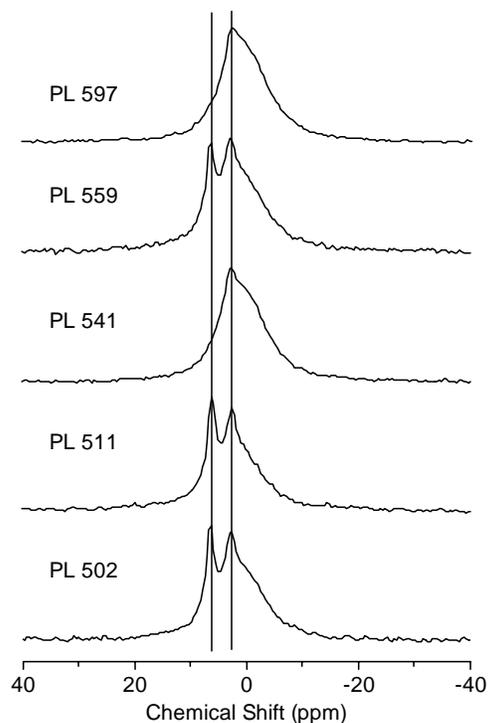
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The management and protection of fresh water supplies is a major global challenge. Because it has been recognized as the limiting nutrient for eutrophication in fresh waters, phosphorus is a key determinant of the availability of fresh water. Although a naturally occurring aging phenomenon of surface water, eutrophication is accelerated by anthropogenic nutrient inputs, and poses a severe threat to water quality worldwide. Elevated concentrations of phosphorus have also been linked to outbreaks in estuaries on the Atlantic Coast of the dinoflagellate *Pfiesteria piscicida*, which produces a toxin lethal to fish and hazardous to humans. Governmental regulation has reduced phosphorus outputs from point sources such as industrial processes and wastewater treatment plants, but large amounts of phosphorus continue to enter the environment from non-point sources such as agricultural operations.

Amendment of fertilizers and farm effluents with aluminum sulfate (alum) has proven



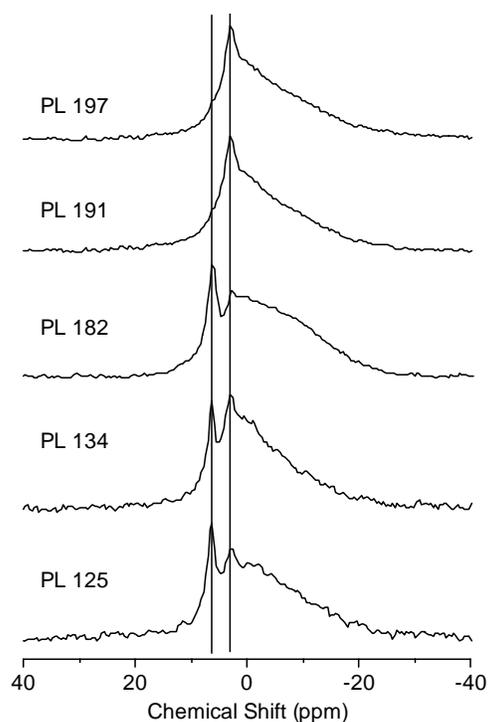
**Figure 1.**  $^{31}\text{P}$  MAS NMR spectra of unamended poultry-litter samples with proton decoupling.

effective in reducing water-soluble phosphorus from agricultural sources. Although demonstrated in the field, little is known about the P-speciation that is the basis for the effectiveness of this practice. This knowledge is important for the evaluation of long-term stability and bioavailability of P, which is needed for an assessment of the sustainability of agricultural operations. Solid-state, magic-angle-spinning  $^{31}\text{P}$  nuclear magnetic resonance (MAS NMR) spectroscopy was used to investigate the P speciation in alum-amended and unamended poultry litter (Hunger et al. 2004). The results indicate the presence of a complex mixture of organic and inorganic orthophosphate phases. A calcium phosphate phase, probably a surface precipitate on calcium carbonate, could be identified in both unamended (Figure 1) and alum-amended poultry litter (Figure 2), as well as phosphate bound by hydrogen bonds to adsorbed water molecules or organic functional groups.

Phosphate associated with Al was found in the alum-amended poultry litter, present either as a poorly ordered wavellite or as phosphate surface complexes on aluminum hydroxide that had been formed by the hydrolysis of alum. However, a complex mixture of organic and inorganic phosphate species could not be resolved. Phosphate associated with Al comprised on average  $40(\pm 14)\%$  of the total P in alum-amended poultry litter, whereas calcium phosphate phases comprised on average  $7(\pm 4)\%$  in the alum-amended poultry litter and  $14(\pm 5)\%$  in the unamended poultry litter.

## Reference

Hunger S, H Cho, JT Sims, and DL Sparks. 2004. "Direct Speciation of Phosphorus in Alum-Amended Poultry Litter: Solid-State  $^{31}\text{P}$  NMR Investigation." *Environmental Science and Technology* 38(3):674-681.



**Figure 2.**  $^{31}\text{P}$  MAS NMR spectra of alum-amended poultry-litter samples with proton decoupling.

## Effects of Rehydration and La Doping on the Thermal Stability of Highly Active Alumina

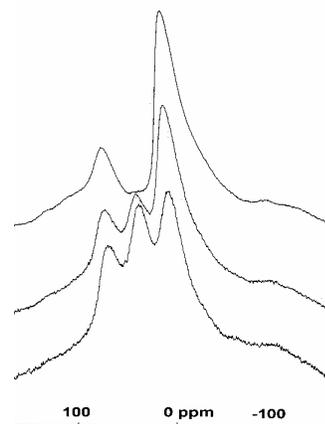
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Mesoporous aluminas are valued in catalysis because they have properties that allow both long life and activity. A compromise must be struck between activity and stability in the development of catalysts, and the hydrolytic stability of alumina is one factor to consider. Previous investigators have shown that a group of highly active aluminas, called “superfive,” contain a substantial fraction of five-coordinate ( $Al^V$ ) aluminum which is susceptible to crystallization and loss of activity (Coster et al. 1995). Nuclear magnetic resonance (NMR) experiments using the Varian Infinity 300 MHz instrument in the W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL) confirmed the presence of  $Al^V$  in alumina prepared by a new method developed at the University of Arkansas at Little Rock (Wilcox et al. 2003). Interest in improving the stability of our aluminas led to further NMR experiments. To prepare samples for these new NMR measurements, synthetic methods were modified and incorporation of  $La^{3+}$  (0.086 mole fraction of La for each mole Al) in some samples was used to inhibit crystallization kinetics.

Figure 3 shows the  $^{27}Al$  magic-angle-spinning NMR (MAS NMR) data for a modified alumina calcined at progressively higher temperatures. The resonances for  $Al^V$ ,  $Al^V$ , and coordinatively saturated  $Al^VI$  occur at about 65, 35, and 0 ppm, respectively. The  $Al^V$  resonance of the alumina was vanquished by 800°C so no improvement in thermal stability over our previous studies was observed. Unfortunately, the La-doped samples exhibited similar spectra to those shown in Figure 3. Since La is proven to inhibit bulk crystallization of alumina, we had hoped that its presence would improve the thermal stability of  $Al^V$  environments. However, because  $Al^V$  environments are attributed to surface species, the benefits of La to bulk properties may not also include surface stabilization.



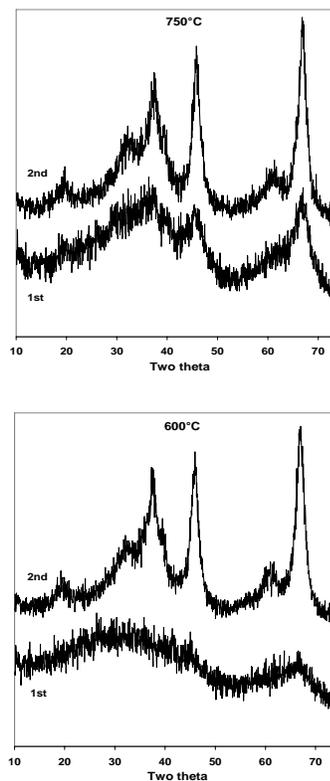
**Figure 3.**  $^{27}Al$  MAS NMR data for active alumina calcined to 400°C, 600°C, and 800°C.

Additional studies were conducted to determine the effects of rehydration on thermal stability. Calcined alumina samples were weighed, exposed to 100% humidity at ambient temperature for three days, reweighed, and re-calcined. Previous studies of “superfive” aluminas indicated that rehydration followed by calcination results in crystallization, a decrease in water adsorption capacity, and a loss of  $Al^V$  species (Coster et al. 1995). These trends were also observed in our samples.

Figure 4 shows the powder x-ray diffraction data obtained before and after hydration and re-calcination. As seen in Figure 4, whereas the samples were amorphous after the first calcination, subsequent treatment converted them to the delta-phase. Regarding the water-adsorption capacity, our samples exhibited a higher pore volume than those reported by Coster and Fripiat 1995 so a greater water capacity was observed. In the best case, a single calcination of a precursor to 600°C for 3 hours gave an alumina that adsorbed 110 wt% of the water. After re-calcining, water-adsorption capacity decreased to 43 wt%. Other samples with a lower capacity after the first calcination retained a higher water-adsorption capacity after re-calcining. The maximum capacity observed for a sample after rehydration/re-calcination was 57 wt%. These results indicate that the most active aluminas are subject to greater deactivation after water exposure.

## References

- Coster D, JJ Fripiat, M Muscas, and A Auroux. 1995. “Effect of Bulk Properties on the Rehydration Behavior of Aluminas.” *Langmuir* 11(7):2615-2620.
- Wilcox L, G Burnside, B Kiranga, R Shekhawat, MK Mazumder, RM Hawk, DA Lindquist, and SD Burton. 2003. “Porous Alumina Prepared from Diethylaluminum Amide, Acetone, and Water.” *Chemistry of Materials* 15(1):51-56.



**Figure 4.** Powder x-ray diffraction of calcined aluminas before and after rehydration/re-calcination.

## The Effect of Water on the Adsorption of NO<sub>2</sub> in Na- and Ba-Y, FAU Zeolites: A Combined FTIR and Temperature-Programmed Desorption Investigation

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The removal of oxides of nitrogen (NO<sub>x</sub>) from automotive exhaust gases is a tremendous challenge to the catalytic community, in particular when the engine is operated under lean conditions (i.e., in excess oxygen, as from diesel engines). Under these conditions, the traditional three-way catalysts do not work due to their very high activity for hydrocarbon oxidation, resulting in the depletion of the reducing agent before NO<sub>x</sub> reduction can take place. Among the most promising new technologies for diesel exhaust aftertreatment are the NO<sub>x</sub> adsorber and non-thermal plasma-assisted catalytic NO<sub>x</sub> reduction. Base metal oxide adsorbers (in particular BaO) have been shown to be highly effective for the removal of NO<sub>x</sub> from an oxygen-rich exhaust gas mixture. Recently, we reported very promising activities for both Na- and Ba-Y, FAU zeolites in the catalytic lean NO<sub>x</sub> reduction, when the catalyst was used in conjunction with a non-thermal plasma. The two most important reactions that take place in the plasma are the almost complete conversion of NO to NO<sub>2</sub>, and the formation of partially oxidized hydrocarbon species (e.g., acetaldehyde) in significant quantities. Combining the strong oxidizing power of NO<sub>2</sub> and the ease of oxidizability of CH<sub>3</sub>CHO results in a high level of NO<sub>x</sub> reduction over these base zeolite catalysts at relatively low temperatures (~473 K).

We previously reported that exchanging the charge-compensating Na<sup>+</sup> ions for Ba<sup>2+</sup> ions in Y,FAU (Y) zeolites increases the NO<sub>x</sub> conversion by more than 10% and also widens the temperature window in which high activity can be sustained. We have suggested that one possible explanation for this activity enhancement was the stronger adsorption of NO<sub>2</sub> observed over Ba-Y in comparison to Na-Y. Here, we report on our recent finding on the adsorption of NO<sub>2</sub> on both Na- and Ba-Y. We used Fourier transform infrared spectroscopy to identify the nature of adsorbed species, and correlated those findings with the results obtained from temperature-programmed desorption (TPD) of NO<sub>2</sub>. The adsorption and desorption of NO<sub>2</sub> were investigated on both water-free (dry) and water-containing (wet) catalysts.

The interaction of NO<sub>2</sub> with both Na- and Ba-Y, FAU zeolites resulted in the formation of the same type of ionic species. In the absence of adsorbed water, NO<sup>+</sup> ions formed by the disproportionation of NO<sub>2</sub> are adsorbed onto framework O<sup>-</sup> sites associated with the charge-compensating cationic positions of the zeolite, while NO<sub>3</sub><sup>-</sup> ions are bound to the charge-compensating cations. At high NO<sub>2</sub> dosages, NO+NO<sub>2</sub> adducts can form on both catalysts. The thermal stabilities of these adsorbed NO<sub>x</sub> species strongly depend on the nature of the charge-compensating cation. The adsorption of these species is much weaker over Na-Y as a large fraction of the NO<sup>+</sup> and NO<sub>3</sub><sup>-</sup> desorb even upon evacuation at 295 K. On the other hand, all the adsorbed NO<sub>x</sub> species are much more stable over Ba-Y, so much so that even most of the NO+NO<sub>2</sub> species are present on this catalyst following room

temperature evacuation. The presence of water dramatically influences the adsorption of  $\text{NO}_2$  on both materials, as it competes for the available adsorption sites and also reacts with some of the adsorbed  $\text{NO}_x$  species. The number of adsorbed  $\text{NO}^+$  species decrease with increasing amounts of  $\text{H}_2\text{O}$ , and  $\text{HNO}_x$  species are formed that interact with the charge-compensating cation forms zeolitic  $-\text{O}-\text{H}$  groups and  $\text{Mn}+(\text{NO}_x)_n$ . The  $\text{NO}_2$  TPD feature in Na-Y shifts from 350 K to 520 K, while on Ba-Y the corresponding TPD feature shifts from 470 K to 670 K. The effect of water on the adsorption of  $\text{NO}_2$  on Ba-Y is shown in Figure 5. The series of TPD spectra were obtained at a constant level of  $\text{NO}_2$  dosing while varying the amount of water preadsorbed onto the Ba-Y sample. The series infrared spectra were recorded by gradually increasing the amount of water added to an  $\text{NO}_{2,\text{ads.}}$ -Ba-Y sample. The large differences found here in the stabilities of adsorbed  $\text{NO}_x$  species over these two catalysts seem to strongly correlate with their vastly different catalytic activities observed in the non-thermal plasma-assisted  $\text{NO}_x$  reduction.

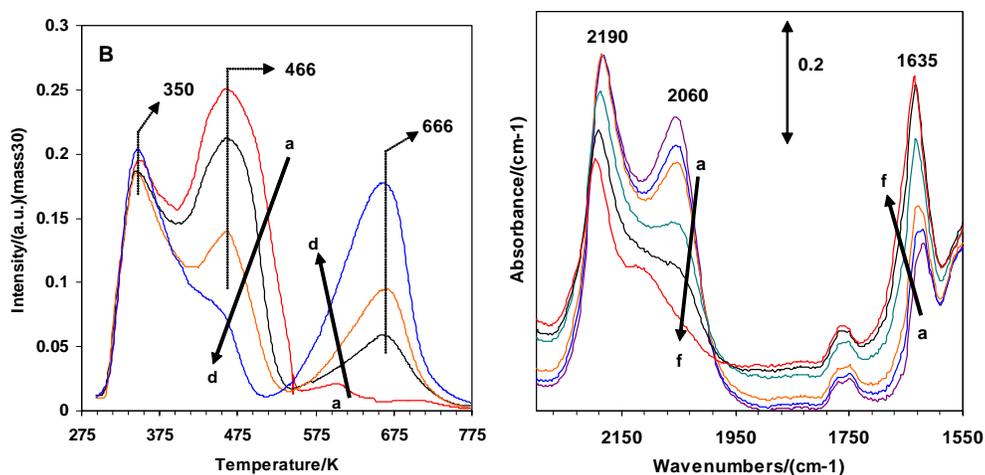


Figure 5. The effect of  $\text{H}_2\text{O}$  on the adsorption of  $\text{NO}_2$  over Ba-Y.

## Investigation of Cr as an Alternative Adhesion Layer in Pt/Si Electrodes for Ferroelectric Perovskites

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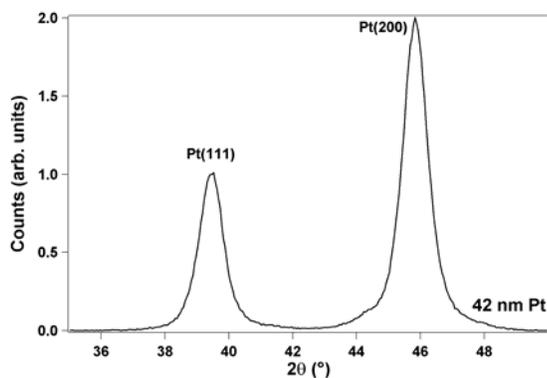
(a) Pacific Northwest National Laboratory, Richland, Washington

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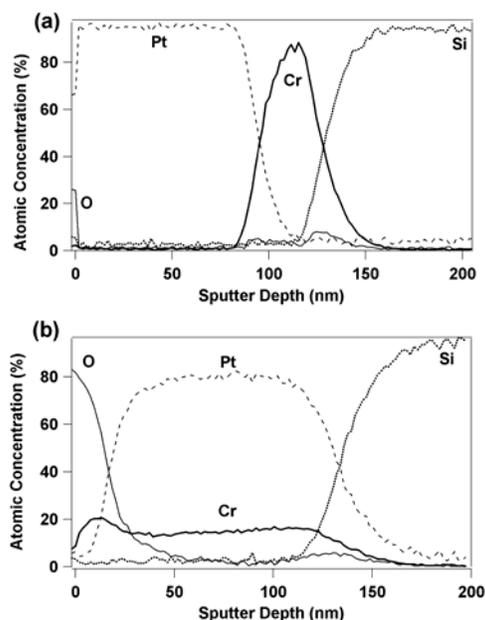
(d) Intel Corporation, Santa Clara, California

The deposition of thin film perovskites such as  $(\text{Ba,Sr})\text{TiO}_3$  and  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  on conducting electrodes is technologically relevant for microelectronics applications such as dynamic random access memory and non-volatile ferroelectric random access memory. Platinum is often chosen as the bottom electrode material due to its oxidation resistance during subsequent perovskite film deposition. When polycrystalline platinum thin films are deposited on  $\text{Si}(001)$  or  $\text{SiO}_2/\text{Si}(001)$ , it is necessary to include a thin layer of another material at the interface to improve platinum adhesion. Titanium is the most common adhesion layer, although  $\text{TiO}_2$ , Ta,  $\text{ZrO}_2$ , and TiN have also been investigated. Since these adhesion materials are not lattice-matched to platinum, the resulting platinum film is polycrystalline with a strong (111) orientation. It is desirable to deposit perovskites with (100) orientation, and a close lattice match exists between  $\text{Pt}(100)$  and both  $(\text{Ba,Sr})\text{TiO}_3(100)$  and  $\text{Pb}(\text{Zr,Ti})\text{O}_3(100)$ . In this study, to enhance the formation of



**Figure 6.** X-ray diffraction pattern of 42-nm platinum / 30 nm chromium /  $\text{Si}(001)$ . After background subtraction, the pattern was normalized to the  $\text{Pt}(111)$  peak height. A significant proportion of  $\text{Pt}(100)$  can be realized with a chromium adhesion layer.

Pt(100) during sputter deposition, chromium was explored as an alternative adhesion layer due to the close lattice match between Cr(100) and Pt(100). It was found that cubic chromium nucleated and stabilized Pt(100) in addition to the low-energy surface Pt(111), to a platinum thickness of 40 to 60 nm. Past this critical thickness Pt(111) dominated the growth. Thin platinum films (42 nm) could be deposited with a significant fraction of Pt(100), as observed by x-ray diffraction (Figure 6). The behavior of the platinum/chromium/silicon electrode structure at elevated temperatures in an oxygen ambient is important for perovskite film deposition. The platinum surface was found to form hillocks after thermal cycling as a stress relief mechanism. In addition, Auger electron spectroscopy depth profiling of films processed under ferroelectric processing conditions indicated chromium diffused into the platinum film, resulting in a thick  $\text{CrO}_x$  layer on the platinum surface (Figure 7). Thus, this thermal instability makes chromium an unsuitable adhesion layer for platinum electrodes.



**Figure 7.** Auger electron spectroscopy depth profiles of 50-nm platinum / 30-nm chromium / Si(001), given as atomic concentration. (a) As-deposited electrode structure. No diffusion is observed. (b) After annealing at 530°C for 60 minutes in 80 sccm  $\text{O}_2$ . Chromium diffusion into the platinum film is observed, as well as a thick layer of  $\text{CrO}_x$  at the platinum surface.

## Nanoparticle-Structured Electrochemical Sensor for Detection of Metal Ions

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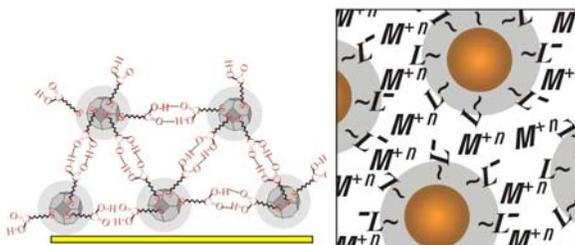
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Recent progress in the area of nanostructured materials has led to the exploration of many potential technological applications such as catalysis, microelectronics, and chemical or biological recognition. One class of nanomaterials consists of core-shell-type nanoparticles with metal or oxide nanocrystal cores and organic shell encapsulation. These nanomaterials can be prepared with high monodispersity of size, enhanced stability, and chemical

tunability. The use of such materials as building blocks toward a molecularly wired three-dimensional ligand framework could find applications in chemical and biological sensing with enhanced interfacial sensitivity and specificity. To exploit the nanostructured materials as active components in electroanalysis, a challenging issue is how to control the ligand framework and interparticle spatial properties. We have been exploring a general strategy that entails core-shell manipulation of gold and alloy nanoparticles as building blocks towards responsive or fine-tuned interfacial materials for electroanalytical applications. Figure 8A illustrates one example system that can be prepared from gold nanoparticles and carboxylic acid functionalized alkyl thiol linkers via hydrogen-bonding linkages through an exchange-crosslinking-precipitation reaction pathway. Such a nanostructured network could lead to a spatially defined ligand framework in which void space forms channels with the nanometer-sized cores defining its size and the shell structures defining its chemical specificity (e.g., L<sup>-</sup> groups provide binding sites to metal ions, M<sup>+n</sup>, see Figure 8B).

We have shown that the nanostructured thin film could be used as an electrode coating that is responsive to electroactive metal ions. The cyclic voltammetric (CV) data (Figure 9) for a nanostructured film of 11-mercaptoundecanoic acid-linked gold nanoparticles of 2-nm core size (MUA-Au<sub>2-nm</sub>) after transferring the thin film electrode from a previous exposure to Cu<sup>2+</sup> (10 mM) solution to a 0.5 M KCl solution revealed the presence of the voltammetric waves associated with the redox reaction of copper. The observation of the electroactivity provides evidence for the incorporation of Cu<sup>2+</sup> into the film. The broadening of the anodic wave is also reflected by the difference in peak current between the reduction (70 μA) and the oxidation (30 μA) waves. The broad reduction wave is largely due to the formation of copper crystals in the film. The observation of the incorporation of Cu<sup>2+</sup> demonstrates that



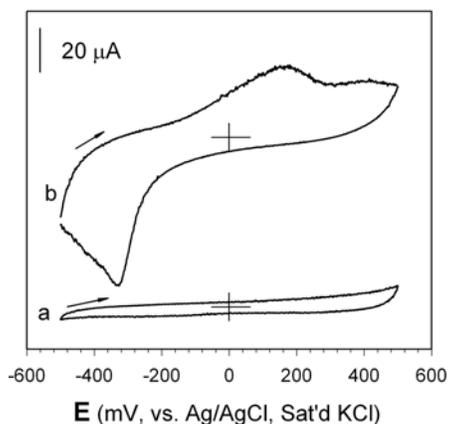
**Figure 8.** Schematic illustrations for (A) the carboxylic acid hydrogen-bonding linked nanoparticle assembly, and (B) the nanostructured ligand (L) framework for sensing metal ions (M).

the nanostructured film could be used for preconcentration of metal ions, which is an area of great interest for current enhancement, as often reported for polymer-modified electrodes based on electrostatic interactions.

The nanostructure-loaded  $\text{Cu}^{2+}$  ions can also be released by pH manipulation of the electrolyte solution. The experiments involved exposure of the thin film electrode to an aqueous solution containing  $\text{Cu}^{2+}$  ions (1 mM) and followed by treatment with a solution of pH = 2. The integrated charges from the CV data (Q) for the  $\text{Cu}^{2+}$ -loaded film were  $25.8^\circ\text{C}/\text{cm}^2$  for oxidation and  $120.4^\circ\text{C}/\text{cm}^2$  for the reduction wave, respectively. After the low pH treatment, these charges were greatly reduced to  $1.9^\circ\text{C}/\text{cm}^2$  for the oxidation and  $5.1^\circ\text{C}/\text{cm}^2$  for the reduction peaks respectively. This is a strong indication that the incorporated  $\text{Cu}^{2+}$  ions are released in the low pH solution. At low pH, the protonation of carboxylic acid groups weakens the binding of the  $\text{Cu}^{2+}$  ions in the film. The large difference between the quantity of charge in oxidation and reduction is indicative of the formation of copper crystals in the film, and therefore oxidation is much slower due to the sluggishness of diffusion across the film. The films were found to be stable over long periods of use and can be regenerated by being immersed in solutions of pH 2.

The viability of loading metal ions into the nanostructure was further demonstrated by determination of the interfacial mass fluxes associated with the redox activity using a copper-loaded nanostructure as a model system. The MUA- $\text{Au}_{2\text{-nm}}$  thin film was coated on the piezoelectrode and preloaded with  $\text{Cu}^{2+}$ . The electrochemical quartz crystal nanobalance data revealed a mass change that was chemically reversible. The mass increases in the reduction sweep, and decreases in the oxidation sweep. This behavior is indicative of mass loading and releasing of ionic species into and out of the film. The presence of  $\text{Cu}^{2+}$  in the Cu-loaded MUA- $\text{Au}_{2\text{-nm}}$  film was further confirmed by x-ray photoelectron spectroscopy and infrared spectroscopy analyses of the surface composition and structure. The results support the qualitative conclusion that  $\text{Cu}^{2+}$  ions are incorporated into the film via  $\text{CO}_2^- - \text{Cu}^{2+}$  complexation.

In summary, we have shown that the nanostructured thin film assemblies derived from gold nanoparticles of 2-nm core size and 11-mercaptopundecanoic acid linker exhibit membrane-like properties. In these films, the hydrogen-bonding-linked interparticle channels can be tuned by pH, electrode potential, and metal loading. The films are shown to be electrochemically responsive to copper ions, which involves  $\text{CO}_2^- - \text{Cu}^{2+}$  binding chemistry in the three-dimensional network. For selective sensing of a target metal ion, the three-dimensional network can be fine-tuned by incorporating a specially designed ligand. These findings have important implications to the design of nanostructured electrochemical sensors for selective monitoring of metal ions in environmental samples.



**Figure 9.** CV curves for MUA- $\text{Au}_{2\text{-nm}}$ /GC electrode in 0.5 M KCl. (a) before exposure to  $\text{Cu}^{2+}$  and (b) after exposure to 10 mM  $\text{Cu}^{2+}$  / 0.5 M KCl for 10 mins. ( $0.28 \text{ cm}^2$ ,  $50 \text{ mV/s}$ ).

## Surface-Induced Dissociation of Ions Produced by Matrix-Assisted Laser Desorption/Ionization in a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer

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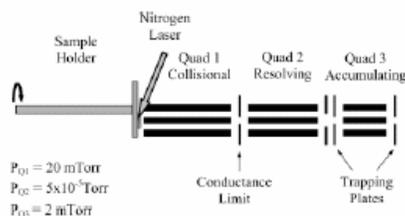
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Large molecules can be introduced into the gas phase using soft ionization techniques such as electrospray ionization or matrix-assisted laser desorption/ionization (MALDI) (Figure 10) and mass-analyzed using a variety of mass spectrometric approaches. Although accurate mass measurement is an important prerequisite for mass spectrometric analysis of peptides and proteins—the focus of proteomics—it is not sufficient for unambiguous identification of these large molecules. For this reason, tandem mass spectrometry, based on structure-specific fragmentation of gas-phase ions, is a critical step for peptide and protein sequencing and identification. Because of the soft nature of electrospray ionization and MALDI, fragmentation of ions produced using these techniques requires a separate ion activation step, in which the internal energy of the ion is increased by collisions with a neutral gas or with a surface, multiphoton absorption, or electron attachment. It is well established that dissociation of gas-phase peptides and proteins is a strong function of their charge state.

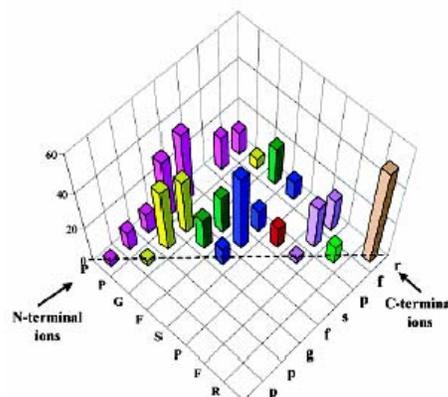
The combination of MALDI with Fourier transform ion cyclotron resonance (FTICR) mass spectrometry offers very high mass resolution and mass accuracy as well as multiple stages of tandem mass spectrometry (MS<sub>n</sub>) that are essential for many applications. However, poor fragmentation patterns commonly obtained for MALDI ions using conventional ion activation techniques in FTICR mass spectrometry, such as sustained off-resonance irradiation (SORICID) or infrared multiphoton dissociation, limit the utility of this combination for structural characterization of biomolecules.

In this work, the utility of surface-induced dissociation (SID) is evaluated. These detailed studies of the kinetics and dynamics of SID of singly protonated ions (generated using electrospray ionization) in FTICR mass spectrometry revealed that at low collision energies, ion activation by collisions with surfaces closely mimics multiple-collision activation in the gas phase. A clear indication for this finding is the striking similarity between SORICID and low-energy SID spectra obtained for both small and large peptides. At high collision energies, we observed a transition in the dynamics of ion-surface interaction attributed to instantaneous dissociation of ions on the surfaces, shattering the transition. Shattering results in opening up a variety of dissociation pathways that cannot be achieved by slow activation methods. The shattering transition is particularly pronounced for arginine-containing peptides that fragment selectively at low collision energies.



**Figure 10.** Schematic view of the intermediate-pressure MALDI source.

The first results on SID of MALDI-generated ions in FTICR mass spectrometry demonstrated unique advantages of SID over SORICID for structural characterization of singly protonated peptide ions. As expected based on our prior experience, both slow activation by gas-phase collisions (SORICID) and fast excitation of ions by collisions with surfaces at relatively low collision energies provide similar fragmentation patterns. However, at higher collision energies, SID fragmentation of peptide ions is dominated by shattering, resulting in formation of a large number of sequence-specific fragment ions. Although the transition from recoil (slow decay) to shattering (fast decay) is a fairly sharp function of the internal energy of the ion, ion-surface impact results in deposition of a distribution of internal energies into the ensemble of ions that effectively mixes the slow and fast decay in the resulting SID spectrum (Figure 11).



**Figure 11.** Backbone fragmentation map for the 55-eV SID of des-Arg1-bradykinin. The capital letters denote the N-terminal amino acid residue in the fragment ion sequence, and the lowercase letters correspond to the C-terminal amino acid residue.

This work took additional advantage of a wide internal energy distribution of ions resulting from collision with a stiff diamond surface, a process that provides a better mixing of slow and fast fragmentation channels. The SID results demonstrate a significantly better sequence coverage for singly protonated ions that are difficult to fragment using conventional ion activation techniques in FTICR mass spectrometry. It follows that the combination of SID with MALDI FTICR mass spectrometry is a new powerful method for characterization and identification of biomolecules. A full discussion of this work appears in Laskin et al. 2004.

## Reference

Laskin J, KM Beck, JJ Hache, and JH Futrell. 2004. "Surface-Induced Dissociation of Ions Produced by Matrix-Assisted Laser Desorption/Ionization in a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer." *Analytical Chemistry* 76(2): 351-356.

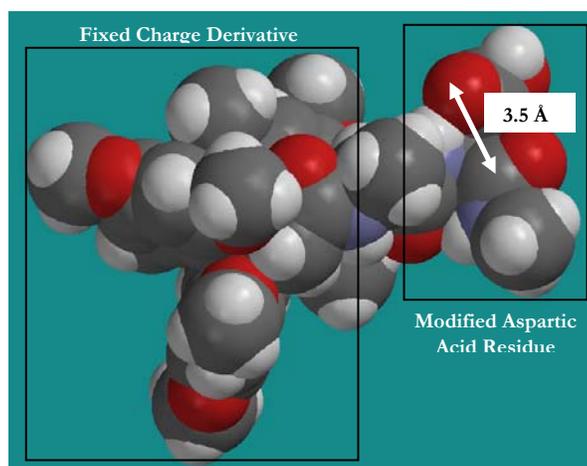
## Computational Investigation of the Fixed Charge Derivative Tris[(2,4,6-trimethoxyphenyl) phosphonium] Electrostatic Potential and the Charge-Remote Aspartic Acid Cleavage Mechanism

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The objective of this project is to computationally investigate the charge-remote peptide cleavage mechanism C-terminal to aspartic acid in the gas phase. Charge-remote fragmentation in the absence of an ionizing proton can be induced by attaching the fixed-charge derivative Tris[(2,4,6-trimethoxyphenyl) phosphonium] (TMPP) to the N-terminus of aspartic acid-containing peptides. Investigation of this fragmentation mechanism is important because the identification of peptides and proteins via tandem mass spectrometry is improved when peptide fragmentation patterns can be accurately predicted. This project applies to the field of proteomics, which has become increasingly more significant in recent years.



**Figure 12.** Computational result demonstrating the lack of H-bonding between the fixed charge derivative and the modified aspartic acid residue, and the close vicinity (3.5 Å) of the nucleophilic oxygen to the electrophilic carbon.

Mass spectrometry is one way to identify proteins in a complex sample, typically via protein digestion followed by liquid chromatographic separation and tandem mass spectrometry analysis of the resulting peptides. The large volume of data collected from this type of analysis is sorted and analyzed by a sequencing algorithm. Although this method is currently being used successfully in a high-throughput manner, the sequencing algorithm can be improved with a better fundamental understanding of why peptides fragment in certain ways, as prediction of the fragmentation pattern is an important part of the algorithm.

The presence of aspartic acid in a peptide causes preferential fragmentation patterns, thereby reducing the probability of peptide identification by current sequencing algorithms. Aspartic acid tends to cleave preferentially on its C-terminal side. This selective cleavage is more prominent when the number of ionizing protons does not exceed the number of arginines present in the peptide. This observation is significant because the enzyme trypsin is

commonly used to digest proteins, leading to a significant number of arginine-containing peptides that are analyzed for identification by tandem mass spectrometry.

Selective cleavage data suggest that aspartic acid fragments via a charge-remote mechanism because when the proton is sequestered at the basic arginine side chain, cleavage at aspartic acid is preferentially observed. When a mobile proton is available, cleavage is randomized, with many cleavages along the peptide backbone observed. This phenomenon was further investigated by attaching the fixed-charge derivative TMPP to the N-terminus of aspartic acid containing peptides. Presumably, cleavages along the peptide backbone will take place via a charge-remote process because of the absence of a mobile ionizing proton. Selective cleavage at aspartic acid is observed when the fixed-charge derivative is present, but when an additional proton is added, charge-directed cleavages along the peptide backbone are also prominent.

Computational modeling was recently undertaken at PNNL to rule out direct interaction between the charge-carrying TMPP group and aspartic acid. Initially, the optimized structure and electrostatic potential of TMPP terminated with a methyl group was calculated. These modeling results verify most positive charge is buried within the TMPP derivative near the charged phosphorus atom. Therefore, it is presumed this positive charge will be unable to influence the cleavage of an aspartic acid on an attached peptide in a charge-directed manner.

In addition, the structure of TMPP attached to a small peptide, Ala-Asp, was computationally investigated (Figure 12). The C-terminal hydroxyl of the Ala-Asp peptide was replaced with methyl to simulate a continuing peptide chain. Results demonstrate the fixed-charge derivative does not interact via hydrogen bonding with the nucleophilic oxygen of the aspartic acid residue, and therefore is not influencing cleavage at that site. Results also show the aspartic acid nucleophilic oxygen lies approximately 3.5 Å away from the electrophilic carbon, a reasonable distance for nucleophilic attack. Currently, calculations are under way to locate the transition state for the charge-remote aspartic acid cleavage mechanism.

## Large-Scale Code Development Applied to Building a Geometry-Based Computational Framework for Biology and Ecology Applications

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*(a) Pacific Northwest National Laboratory, Richland, Washington*

*(b) Computational Geometry Consultants, Placitas, New Mexico*

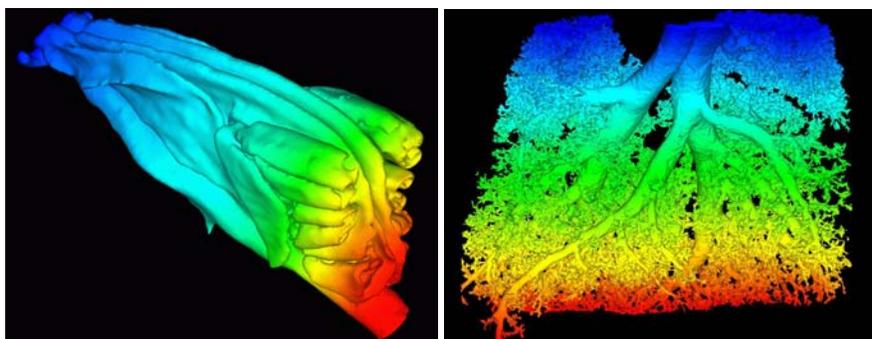
*(c) University of Connecticut Health Center, Farmington, Connecticut*

*(d) Pittsburgh SuperComputing Center, Pittsburgh, Pennsylvania*

*(e) Salk Institute, La Jolla, California*

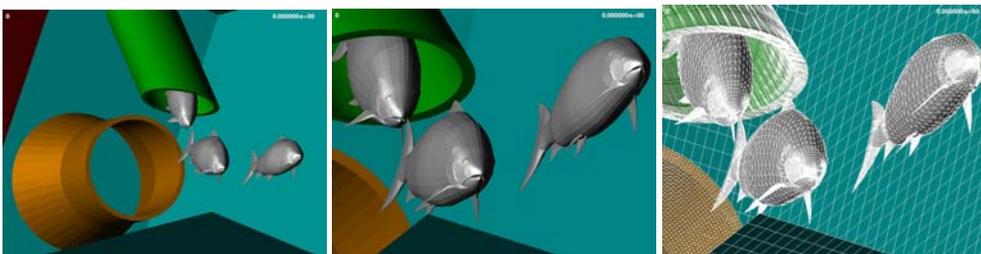
Geometry-based computational biology and ecology applications involve scale lengths in time and space that span many orders of magnitude, making them truly multiscale and very difficult to model. The entire area of computational biology could benefit from access to a geometry-based modeling capability that is adaptive in space and time such that it could capture aspects of multiscale geometry and time-dependent computational physics features. In this project, we propose to use the parallel computational framework of the NWGrid and NWPhys codes to provide adaptive, computational engines as the basis for a geometry-based simulator.

Including explicit three-dimensional geometry into adaptive and time-dependent mesh-based computational physics calculations represents a Grand Challenge problem in any area. Areas where these types of simulations have been in progress for some time include ASCI, atmospheric modeling (weather and climate), engineering (aerospace, automotive, semiconductor), and subsurface modeling (oil and gas and waste migration). Including anatomy and physiology into computational biology simulations for cells, tissues, organs, whole human, or fish has not been attempted partly because these areas have not had access to the computational simulation tools or computational resources necessary to generate the



**Figure 13.** Virtual respiratory system. The left image shows the sinus of the rat, with the nostrils to the left. The image on the right shows the reconstruction of a rat lung.

computational geometry/mesh and run such simulations. However, the codes of NWGrid (<http://www.emsl.pnl.gov/nwgrid/>) and NWPhys (<http://www.emsl.pnl.gov/nwphys/>) can be used to generate the geometry/mesh as well as the computational physics simulations all within a high-speed, parallel, distributed memory environment.



**Figure 14.** Salmon moving through a dam. Computational geometry and meshes on the right show the simulation of three salmon being injected into a high-speed water jet as it emerges from a nozzle into a water tank.

Below are two examples of calculations performed for this project using these two codes. Both examples illustrate geometry reconstructions, three-dimensional mesh generation, and computation simulations.

Figure 13 shows geometries that were reconstructed from nuclear magnetic resonance (NMR) volume data (gathered from EMSL's High Field Magnetic Resonance Facility) of the respiratory system of rats. The NMR image data was segmented using the Digital Data Viewer (<http://www.compgeomco.com>). NWGrid was used to perform the feature extraction and volume mesh generation. The computational physics calculations of the fluid dynamics of air flow throughout the respiratory system, which transports chemical vapor and/or particles, were performed using NWPhys. The first image shows the sinus of the rat, with the nostrils to the left, and the second image shows the reconstruction of the rat lungs.

The computational geometry and meshes on the right of Figure 14 show the simulation of three salmon being injected into a high-speed water jet as it emerges from a nozzle into a water tank. Calculations using NWGrid and NWPhys provide a method for predicting the stress/strain levels that fish might experience based on different jet speeds and correlating these predictions with the environments that salmon might encounter while moving through one of the electric power-generating dams found on the Columbia River system in the northwest United States.

## Third-Order Douglas–Kroll Relativistic Coupled-Cluster Theory through Connected Single, Double, Triple, and Quadruple Substitutions: Applications to Diatomic and Triatomic Hydrides

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

(b) Oak Ridge National Laboratory, Oak Ridge, Tennessee

(c) University of Tokyo, Tokyo, Japan

For this research, we use a combination of the converging electron-correlation methods, the accurate relativistic reference wave functions, and the use of systematic basis sets tailored to the relativistic approximation for diatomic and triatomic molecules containing a diversity of elements. Our objective is to present ultimate theoretical machinery applicable to molecules across the entire periodic table with spectroscopic accuracy. We predict the experimental singlet-triplet separations within 0.02 eV (0.5 kcal/mol) for five triatomic hydrides ( $\text{CH}_2$ ,  $\text{NH}_2^+$ ,  $\text{SiH}_2$ ,  $\text{PH}_2^+$ , and  $\text{AsH}_2^+$ ); the experimental bond lengths within 0.002 Angstrom; rotational constants within  $0.02 \text{ cm}^{-1}$ ; vibration-rotation constants within  $0.01 \text{ cm}^{-1}$ ; centrifugal distortion constants within 2%; harmonic vibration frequencies within  $8 \text{ cm}^{-1}$  (0.4%); anharmonic vibrational constants within  $2 \text{ cm}^{-1}$ ; and dissociation energies within 0.02 eV (0.4 kcal/mol) for 20 diatomic hydrides (BH, CH, NH, OH, FH, AlH, SiH, PH, SH, ClH, GaH, GeH, AsH, SeH, BrH, InH, SnH, SbH, TeH, and IH) containing main-group elements across the second through fifth rows of the periodic table. We use coupled-cluster methods including through and up to the connected single, double, triple, and quadruple substitutions (CCSD, CCSDT, and CCSDTQ) derived and implemented automatically for sequential and parallel executions by an algebraic and symbolic manipulation program TCE (Tensor Contraction Engine) for use in conjunction with a one-component third-order Douglas–Kroll approximation for relativistic corrections.

### Reference

Hirata S, T Yanai, WA de Jong, T Nakajima, and K Hirao. 2004. "Third-order Douglas-Kroll Relativistic Coupled-Cluster Theory through Connected Single, Double, Triple, and Quadruple Substitutions: Applications to Diatomic and Triatomic Hydrides." *Journal of Chemical Physics* 120(7):3297-3310.

## Awards and Recognition

**Federal Laboratory Consortium Award.** PNNL and EMSL staff were honored with the 2004 Federal Laboratory Consortium Award, which recognizes outstanding work in accomplishing technology transfer from the national labs to the public and private sectors. Their electrodynamic ion funnel significantly improves the sensitivity of analytical instruments such as mass spectrometers. Award recipients include Battelle Fellow Richard D. Smith, Harold Udseth, Technical Lead of EMSL's High-Performance Mass Spectrometry Facility, and Keqi Tang and Bruce Harrer, PNNL.

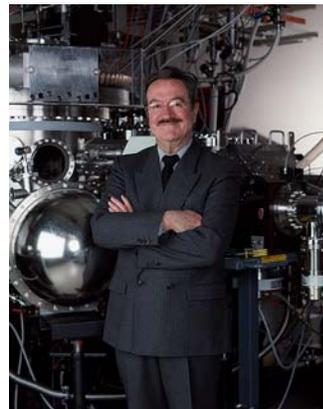
**U.S. Patent.** EMSL researcher Ken Beck and Pacific Northwest National Laboratory researcher David Wunschel were granted U.S. Patent 6,680,477 B2 for an invention that provides a system and process of focusing light to micron and submicron spot sizes for MALDI. The invention features a second process and system for creating a correlated optical image of the ion desorption region of a sample substrate.

**APS Fellow.** Jean Futrell (Figure 15), Battelle Fellow and former EMSL Director, was elected as a Fellow of the American Physical Society (APS). Futrell received his award "For his seminal contributions to the field of mass spectrometry." Election as an APS Fellow is achieved by no more than one half of one percent of the APS membership.

**Systems Engineer of the Year.** Gordon Anderson, Technical Leader of EMSL's Instrument Development Laboratory, was elected by the International Council on Systems Engineering as their 2003 Systems Engineer of the Year. Anderson was recognized for his many contributions to improving systems engineering and implementation (e.g., for systems such as the FTICR MS Proteome Express).

**Outstanding Presentation of Research.** EMSL user Steven Sharpe, Pacific Northwest National Laboratory (PNNL), received an award for his outstanding presentation on PNNL's Infrared Spectral Library. The presentation, given at the National Signatures Program (NSP) Operations Review, resulted in PNNL including its infrared spectra data holdings in NSP's distributed system in order to make the data more widely available to the scientific community. A letter of commendation was provided by Arthur Zuehlke, Deputy Director for Measurement and Signature Intelligence in the Defense Intelligence Agency, to PNNL Director Len Peters about Sharpe's presentation and offer of collaboration.

**E.W. Mueller Award.** Scott Chambers, PNNL Laboratory Fellow and EMSL User, has been selected as the 2004 recipient of the E.W. Mueller award for outstanding research in surface science. He is being recognized for advancing the science of molecular beam epitaxy, and applying it to fundamental investigations of the structural, electronic, and magnetic properties of metal oxide films, surfaces, and interfaces.

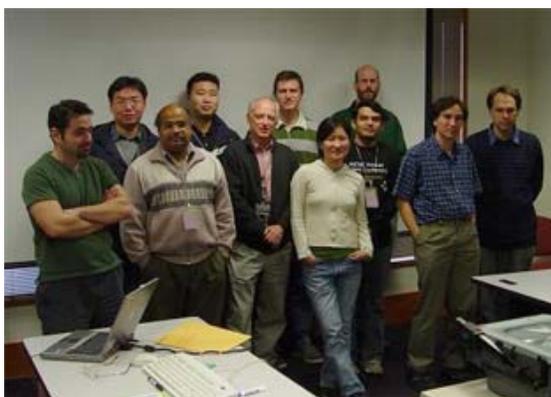


**Figure 15.** Jean Futrell, Director of EMSL from 1998 to 2002, was elected as a Fellow of APS in 2003.

## Professional/Community Service

**2004 AAAS Meeting – Seattle.** Julia White, Technical Lead for EMSL User Services & Outreach, organized an informational workshop featuring EMSL's proteomics mass spectrometry capabilities at this year's American Association for the Advancement of Science Meeting in Seattle, Washington. The AAAS meeting provided a unique opportunity to interact with researchers performing cutting edge work in biology who were curious about the utility of proteomics and the applicability of that approach to their research. Four PNNL scientists presented overviews about EMSL facilities, equipment, and specific research examples: George Michaels and Mary Lipton, PNNL, and Gordon Anderson and Harold Udseth, EMSL.

**Nanoscience Course.** A three-week intensive course, "Synthesis and Characterization of Nanomaterials," was conducted at EMSL (Figure 16). The course, held January 5 – 23, 2004, was the first offering of three courses developed through a National Science Foundation grant "Development of UW-PNNL Collaborative Curriculums in Nanoscience and Technology" and was proposed as part of the Joint Institute for Nanoscience. Fumio Ohuchi, University of Washington, Seattle, Washington served as the principal investigator, while PNNL's Don Baer served as coordinator. This course is designed to speed undergraduate and graduate entry into the nanomaterials field and provides students with the opportunity to directly interact with laboratory researchers. Several lectures (17 by PNNL staff and seven by Washington State University, University of Washington, University of Idaho, and University of Alaska faculty) were given on a variety of topics, and small laboratory projects (with mentorship provided by 14 PNNL staff members) were conducted involving synthesis and characterization. Most students indicated that the course was among the more difficult they had taken, but also of high value.



**Figure 16.** Students and instructors of the three-week course on nanomaterials.

Three synthesis activities were conducted as part of this course: the formation of a nanolayer epitaxial  $\text{Cr}_2\text{O}_3$  oxide film, the formation of  $\text{Cu}_2\text{O}$  oxide nanodots, and the formation by sol-gel process of  $\text{CeO}_2$  nanostructured films. These three nanostructured materials were then analyzed using the following EMSL capabilities in EMSL's Interfacial and Nanoscale Science Facility: electron microscopy, such as scanning electron microscopy and transmission electron microscopy; x-ray scattering; electron spectroscopy, such as Auger electron spectroscopy and x-ray photon spectroscopy; ion beam analysis, such as Rutherford backscattering, nuclear reaction analysis, and ion channeling; and scanning probe microscopy, such as atomic force microscopy. Students formulated questions and obtained

the answers for each material, and then participated in a group discussion of the results from the different methods, the consistencies, and the uncertainties.

## Major Facility Upgrades

**Mössbauer Spectrometer Enhancement.** A new closed-cycle cryostat was installed on one of the Mössbauer spectrometers in EMSL's Environmental Spectroscopy and Biogeochemistry Facility to allow variable temperature studies down to 10 K.

**Optical Microscope.** Also in this facility, a Nikon TE-2000U inverted optical microscope was integrated with a SpectraPhysics MOPO-730 nanosecond laser system and an Acton-Research MicroSpec 2156i spectrograph fitted with a Roper Scientific Research Intensified charge-coupled diode detector. Currently, the system is being tested for cryogenic fluorescence studies of heavy metal radionuclide-contaminated (such as uranium, europium and curium) Hanford Site sediments. This system can potentially be used to perform time-resolved fluorescence imaging and to subsequently acquire time-resolved fluorescence spectra of specific areas of interest on the fluorescence image.

**Flow Cell for Fate and Transport Studies.** A new flow cell was designed and constructed for EMSL's Subsurface Flow and Transport Laboratory. The cell is equipped with several monometer ports to measure the buildup of gas pressures. Initial experiments will involve understanding the fate and transport of nitrogen gas produced in situ by indigenous nitrate-reducing organisms.

**Ultrahigh vacuum AFM/STM System.** The Interfacial and Nanoscale Science Facility received from Omicron Associates the components for the state-of-the-art ultrahigh vacuum non-contact atomic force microscopy/scanning tunneling microscopy (AFM/STM) system. Facility staff are currently assembling and installing the system. In addition to the scanning probe capability, this instrumentation will be equipped with x-ray photoelectron and Auger electron spectroscopy; and plasma, sputter cleaning, and deposition capabilities.

**MSCF Expansion and Elan4 Upgrade.** Preliminary design work on the expansion of the Molecular Science Computing Facility (MSCF) continued through January and into early February. Additionally, the parallel filesystem of EMSL's HPCS2 supercomputer was upgraded to use Elan4. This upgrade provides users with much faster access to the global filesystem. Early results of the upgrade demonstrated a sustained "write" rate of over 600 megabytes per second to the global filesystem by each client; before the upgrade, the system demonstrated a write rate of 200 megabytes per second. This three-fold increase will profoundly impact the ability of the system's clusters to perform disk-intensive operations such as bioinformatics and indirect electron structure methods.

## News Coverage

**Planar All-Boron Clusters.** The March 1, 2004, issue of *Chemical & Engineering News* features EMSL users Lai-Sheng Wang, Washington State University-Tri-Cities, Pullman, Washington and Alexander Boldyrev, Utah State University, Logan, Utah in an article on planar all-boron clusters and their derivatives as potential building blocks.

**EMSL Staff Member Authors Column.** Scott Studham, Technical Lead of EMSL's Molecular Science Computing Facility Operations Group, will be writing a regular column for *Scientific Computing & Instrumentation* magazine, starting in February. The first column, appearing February, is entitled "[Rekindle the Fire: Building Supercomputers to Solve Dynamic Problems.](#)"

**E-Broadcast on Modeling and Simulation.** Studham also participated in a live technology e-broadcast conducted by *Scientific Computing & Instrumentation* magazine. Studham and two other panelists addressed the topic "Enhancing Computational Modeling and Simulation with Itanium Technology."

**Computational Grand Challenges.** EMSL's 2005 Call-for-Proposals (for allocations of computer time) for Computational Grand Challenge Applications are now being accepted for environmental molecular science research areas that address the environmental problems and research needs facing DOE and the nation (see <http://mscf.emsl.pnl.gov>). The announcement was featured on several informational web sites.

## Visitors and Users

### Chemistry and Physics of Complex Systems Facility

- Jormarie Alvarez, Purdue University, West Lafayette, Indiana, collaborated with Julia Laskin, Pacific Northwest National Laboratory, Richland, Washington, on the study "Dissociative Charge Inversion of Peptides by Surface-Induced Dissociation."
- Allan Bertram, University of British Columbia, Vancouver, British Columbia, Canada, gave the presentation "Ice Cloud Formation, Phase Transitions of Atmospheric Aerosols, and Heterogeneous Chemistry."
- Craig M. Brown, New York State Department of Health Wadsworth Center, Albany, New York, collaborated with Russ Tonkyn, Pacific Northwest National Laboratory, Richland, Washington, on the study "Inelastic Electron Scattering Cross Section Measurements in Liquid Water."
- Alan Maccarone, University of Colorado, Boulder, Colorado, collaborated with Alan Joly, Pacific Northwest National Laboratory, Richland, Washington, on the study "Second Harmonic Generation from Organic Water/Air Interfaces."

- William F. Morgan, University of Maryland, Baltimore, Maryland, gave the presentation “Non-Targeted Effects of Ionizing Radiation: Genomic Instability and Bystander Effects.”
- Andrew Snyder, University of Maryland, Baltimore, Maryland, worked on the study “Electron-Induced Genomic Instability.”

## Environmental Spectroscopy and Biogeochemistry Facility

- Paul Bagus, University of North Texas, Denton, Texas, and Eugene Ilton, Pacific Northwest National Laboratory, Richland, Washington, collaborated on ab initio calculations for the Cr(III)2p x-ray photon spectroscopy of CrO<sub>6</sub> clusters that represent the garnet structure. These calculations are testing the influence of silicate-bonding environments on the multiplet structure of Cr(III) X-ray photon spectra. Relative energies for multiplet lines have been calculated, with calculations to determine relative multiplet intensities currently running.
- Sue Clark, Washington State University, Pullman, Washington, is spending part of her one-year sabbatical at EMSL working with Andy Felmy, Zheming Wang, and Odeta Qafoku, Pacific Northwest National Laboratory, Richland, Washington (Figure 17). The team is designing experiments to obtain thermodynamic data describing lanthanide and actinide complexation equilibria in mixed solvent systems. Cation solvation-desolvation for these elements is often a driving force in their complexation and sorption reactions. Luminescence spectroscopy is employed to probe cation hydration as a function of solvent, which is then related to differences in solubility and complexation constants as the quantity of bulk water in the solvent system is varied. This data will be used to develop thermodynamic models that predict the binding of metal ions (i.e., Ca and the f-elements) in the microbial outer membrane.
- Hailiang Dong, Miami University, Oxford, Ohio, and EMSL researcher Ravi Kukkadapu are collaborating to study bioreduction of two hydrothermal nontronite clays from southern Australia. These samples differ from each other in site occupancies of Fe(III) ions. The research is intended to quantify the distribution of Fe(III) between tetrahedral and octahedral sites in the pure nontronites; characterize iron-biominerals; and more importantly, follow changes (if possible) in a tetrahedral Fe(III) environment upon bioreduction. Cryogenic Mössbauer spectroscopy is primarily being employed in the study.



**Figure 17.** Sue Clark, Odeta Qafoku, and Andy Felmy.

## High-Field Magnetic Resonance Facility

- Cheryl H. Arrowsmith, University of Toronto, Toronto, Ontario, Canada, sent samples to be run on the 600-MHz and 500-MHz spectrometers for the study “Structural Proteomics: Annotating the Genome Using 3D Structure.”
- Geoffrey M. Bowers and Garry S. Crosson, Pennsylvania State University, University Park, Pennsylvania, used the 750-MHz spectrometer for the study “High-Field  $^{27}\text{Al}$  Solid-State NMR Studies of Catalytic Zeolites and Weathered Clay Materials.”
- Stephen R. Holbrook and David E. Wemmer, Lawrence Berkeley National Laboratory, Berkeley, California sent samples to be run on the 500-MHz spectrometer for the study “Structural Biology of the Nudix Proteins from the Extremely Radiation-Resistant Bacterium *Deinococcus Radiodurans*.”
- Evan R. Kantrowitz, Boston College, Chestnut Hill, Massachusetts, sent samples to be run on the 800-MHz spectrometer for the study “Probing the Mechanism of the Alkaline Phosphatase Reaction by  $^{67}\text{Zn}$  and  $^{25}\text{Mg}$  NMR.”
- Gaetano T. Montelione and James M. Aramini, Rutgers University, Piscataway, New Jersey, sent samples to be run on the 800-, 600-, and 500-MHz spectrometers for the study “Structural Genomics of Eukaryotic Model Organisms.”
- Xuefeng Ren, Southern Illinois University, Carbondale, Illinois, used the 750- and 600-MHz spectrometers for “NMR Structural Studies of ApoAI/preb-HDL Particles.”
- Frank D. Soennichsen and Kiattawee Choowongkamon, Case Western Reserve University, Cleveland, Ohio, sent samples to be run on the 800-MHz spectrometer for the study “Structure Determination of Membrane Proteins.”
- Suzana K. Straus and Erica A. Tiong, University of British Columbia, Vancouver, British Columbia, Canada, used the 800-MHz spectrometer to run samples for the study “Development of Resolution Enhancement Techniques for the Complete Structure Determination of Fully  $^{13}\text{C}/^{15}\text{N}$ -Labelled Peptides and Proteins Using Solid State NMR.”
- Gabriele Varani and Thomas C. Leeper, University of Washington, Seattle, Washington, sent samples to be run on the 750-MHz spectrometer for the study “Structure of Telomerase RNA and Telomeric Proteins.”

## Interfacial and Nanoscale Science Facility

- Daniel Allred, Steven Tait, Lien Ngo, Aydin Tankut, and Fumio Ohuchi, University of Washington, Seattle, Washington; Myriam Cotten, Pacific Lutheran University, Tacoma, Washington; Alexandre Kouprine, McGill University, Montreal, Quebec, Canada; Saumya Kothari, University of Tulsa, Tulsa, Oklahoma; Jeahuck Lee and Xiquan Cui, Portland State University, Portland, Oregon; and Fraser Wilkinson, Western Washington University, Bellingham, Washington attended the lectures and laboratory classes for the three-week course “Synthesis and Characterization of Nanomaterials.”

- Zsuzsanna Balogh, Washington State University, Pullman, Washington, used EMSL's scanning electron microscopy capabilities to investigate the chemical weathering of minerals.
- Soo Yin Chin, University of South Carolina, Columbia, South Carolina, used the capabilities in EMSL's catalysis laboratory and surface analytical laboratory to develop new catalytic materials.
- Lisa Edge, Pennsylvania State University, State College, Pennsylvania, used the capabilities in EMSL's oxygen plasma-assisted molecular beam epitaxy facility to investigate the band offsets of  $\text{LaAlO}_3$  films grown on silicon substrates.
- Kelli Griffin, University of Washington, Seattle, Washington, used the capabilities of EMSL's electron microscopy suite and the accelerator facility to characterize Co-TiO<sub>2</sub> films grown by sputter deposition.
- Gary Hansen, Karl Hibbits, and Tom McCord, University of Washington, Seattle, Washington, and Patricia Beauchamp, Jet Propulsion Laboratory, Pasadena, California, used the capabilities in EMSL's accelerator facility to study the MeV ion radiation effects on candidate compositional analogues of surface non-ice materials of the Galilean satellites Europa, Callisto, and Ganymede.
- Allen Johnson, John Farley, Daniel Koury, Denise Parsons, Thao Ho, and Umar Younas, University of Nevada, Las Vegas, Las Vegas, Nevada, and Eric Loewen, Idaho National Engineering and Energy Laboratory, Idaho Falls, Idaho, used the capabilities in EMSL's surface analytical laboratory to investigate the corrosion of materials by lead alloys for advanced reactor and nuclear waste amelioration applications.
- Jie Lian, University of Michigan, Ann Arbor, Michigan, used the capabilities in EMSL's surface analytical laboratory to characterize irradiated and unirradiated pyrochlore materials using x-ray photoelectron spectroscopy.
- Saravanamuthu Maheswaran, University of Western Sydney, Sydney, Australia, used the capabilities in EMSL's accelerator facility to investigate trace arsenic in drinking water using proton-induced x-ray emission. He also attended the three-week course "Synthesis and Characterization of Nanomaterials."
- Velu Subramani, Pennsylvania State University, University Park, Pennsylvania, used the capabilities in EMSL's catalysis laboratory and surface analytical laboratory to study oxidation, reduction, and characterization of new catalytic materials to reform methanol.
- Daqing Zhang and Abdullah Alkateeb, University of Idaho, Moscow, Idaho, used EMSL's atomic force microscope to investigate SiC nanostructures.

## Molecular Sciences Software - New User Agreements with NWChem/Ecce

- Academia Sinica, Beijing, China
- Anderson Asphalt, Shatin, Hong Kong
- Beijing University of Chemical Technology, Beijing, China
- Central Michigan University, Mount Pleasant, Michigan
- CEA Saclay, Gif-sur-Yvette, France
- Center of Photochemistry, Russian Academy of Sciences, Moscow, Russia
- Denison University, Granville, Ohio
- EPFL Swiss Federal Institute of Technology Institution, Lausanne, Switzerland
- Instituto de Tecnologia Quimica Biologica, Oeiras, Portugal
- IRSAMC – Universite Paul Sabati, Toulouse, France
- IPCF-Istituto per I ProcessiChimico-Fisici, Ghezzeno, Italy
- J. Heyrovsky Institute of Physical Chemistry, Academy of Science of the Czech Republic, Prague, Czech Republic
- Kafkas Universitesi, Kars, Turkey
- Lawrence Berkeley National Laboratory, Berkeley, California
- Mayo Foundation, Rochester, Minnesota
- Nankai University, Tianjin, China
- Nanyang Technological University, Singapore
- National Institute for Nanotechnology, NRC Canada, Edmonton, Alberta, Canada
- National University of Ireland, Galway, Ireland
- National Yang-Ming University, Taipei, Taiwan
- Naval Research Laboratory, Stennis Space Center, Mississippi
- NEC Solutions America, Austin, Texas
- RMC Software Inc., Fort Collins, Colorado
- Seoul National University, Seoul, Korea
- The Royal Institution of Great Britain, London, England
- Tokyo Institute of Technology, Tokyo, Japan
- Universidad Autonoma del Estado Morelos, Cuernavaca, Mexico
- Universidad Nacional Autonoma de Mexico, Cuernavaca, Mexico
- University of Erlangen Nürnberg, Erlangen, Germany
- Universitat Jaume I, Castello, Spain
- University of Alabama, Tuscaloosa, Alabama
- University of Alabama at Birmingham, Birmingham, Alabama
- University of California, Merced, Merced, California
- University of California, Santa Barbara, Santa Barbara, California
- University of Manchester, Manchester, United Kingdom
- University of New South Wales, Kensington, Australia
- University of Sydney, Sydney, Australia
- University of Tartu, Tartu, Estonia
- University of Tasmania, Hobart, Australia

## Publications

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

Andrews L, B Liang, J Li, and BE Bursten. 2003. "Noble Gas--Actinide Complexes of the CUO Molecule with Multiple Ar, Kr, and Xe Atoms in Noble-Gas Matrices." *Journal of the American Chemical Society* 125(10):3126-3139.

Beck KM, AG Joly, NF Dupuis, P Perozzo, WP Hess, PV Sushko, and AL Shluger. 2004. "Laser Control of Product Electronic State: Desorption From Alkali Halides." *Journal of Chemical Physics* 120(5):2456-2463.

Bowman MK, EA Berry, AG Roberts, and DM Kramer. 2004. "Orientation of the g-Tensor Axes of the Rieske Subunit in the Cytochrome *bc<sub>1</sub>* Complex." *Biochemistry* 43(2):430-436.

Chen W, AG Joly, JO Malm, and JO Bovin. 2004. "Upconversion Luminescence of Eu<sup>3+</sup> and Mn<sup>2+</sup> in ZnS:Mn<sup>2+</sup>, Eu<sup>3+</sup> Codoped Nanoparticles." *Journal of Applied Physics* 95(2):667-672.

Daschbach JL, BM Peden, RS Smith, and BD Kay. 2004. "Adsorption, Desorption, and Clustering of H<sub>2</sub>O on Pt(111)." *Journal of Chemical Physics* 120(3):1516-1523.

Disselkamp RS, KM Judd, TR Hart, CHF Peden, GJ Posakony, and LJ Bond. 2004. "A Comparison Between Conventional and Ultrasound-Mediated Heterogeneous Catalysis: Hydrogenation of 3-buten-1-ol Aqueous Solutions." *Journal of Catalysis* 221(2):347-353.

Donley MS, RA Mantz, AN Khramov, V Balbyshev, LS Kasten, and DJ Gaspar. 2003. "The Self-Assembled Nanophase Particle (SNAP) Process: A Nanoscience Approach to Coatings." *Progress in Organic Coatings* 47(3-4):401-415.

Edge LF, DG Schlom, SA Chambers, E Cicerrella, JL Freeouf, B Hollander, and J Schubert. 2004. "Measurement of the Band Offsets Between Amorphous LaAlO<sub>3</sub> and Silicon." *Applied Physics Letters* 84(5):726-728.

Foster NS, SE Thompson, NB Valentine, JE Amonette, and TJ Johnson. 2004. "Identification of Sporulated and Vegetative Bacteria using Statistical Analysis of Fourier Transform Mid-Infrared Transmission Data." *Applied Spectroscopy* 58(2):203-211.

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## Presentations

Although not an inclusive list, the following illustrates the variety of topics presented by staff members and users at meetings and events. EMSL does not typically collect presentation information from users external to the laboratory.

Felix EJ. 2004. "Linux Clusters in the Real World/Lustre in that World." Presented by Evan Felix at the LinuxWorld Conference and Expo, New York, New York, on January 21, 2004.

Felix EJ. 2004. "What it Takes to Build a Top 5 Supercomputer Using Linux." Presented by Evan Felix at the LinuxWorld Conference and Expo, New York, New York, on January 22, 2004.

Felix EJ. 2004. "Lustre Use at PNNL; Past, Present and Future." Presented by Evan Felix at the Lustre User Group, Maui, Hawaii, on February 5, 2004.

Hirata S. 2004 "First-Principle Quantum Chemical Calculations of Polymers." Presented by So Hirata at the 2004 Sanibel Symposium in St. Augustine, Florida, on March 1, 2004.

Hirata S. 2004. "'Computational' Spectroscopy for Molecules and Polymers." Presented by So Hirata at the University of Michigan - Biological Modeling Seminar Series in East Lansing, Michigan, on February 13, 2004.

Holtom GR, SD Colson, and Y Zheng. 2004. "Non-Linear Optical Imaging of Living Systems." Presented by Gary Holtom at the NIBIB Sponsored Workshop on Optical Imaging, Bethesda, Maryland, on February 10, 2004.

Resat MS, and GA Kimmel. 2004. "Low-LET Microbeam Investigation of the Track End Dependence of Electron Induced Damage in Normal Human Diploid Fibroblasts." Presented by Marianne Resat (Invited Speaker) at American Association for Cancer Research, Dana Point, California on February 17, 2004.

Zhang Y. 2004. "Damage Accumulation and Defect Relaxation in 4H Silicon-Carbide." Presented by Yanwen Zhang (Invited Speaker) at Uppsala University, Uppsala, Sweden, on February 13, 2004.

Zhang Y. 2004. "Radiation Behavior of Pyrochlores for Immobilizing High-Level Nuclear Waste." Presented by Yanwen Zhang (Invited Speaker) at Lund University, Lund, Sweden, on February 10, 2004.