

EMSL Report
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Research Highlights

Computational Study of Polycyclic Aromatic Hydrocarbons and Their Derivatives

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Polycyclic aromatic hydrocarbons (PAHs) and their ions are key molecular species in many branches of chemistry, such as interstellar, combustion, environmental, and materials chemistry. These species are strong candidates for the carriers of interstellar infrared emission features and diffuse interstellar visible absorption bands, and are thought to be a major carbon reservoir in the interstellar medium. They are also primary intermediate species that form in combustion processes and are the most ubiquitous environmental contaminants from natural and manmade sources with varied mutagenic and carcinogenic activities. It has been proposed that PAHs are the precursors of flame-produced soot and fullerenes.

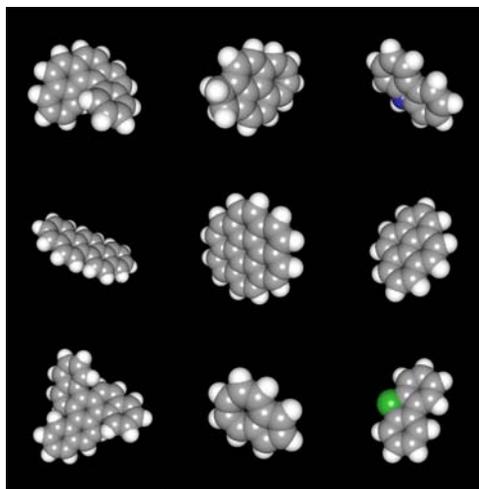


Figure 1. Some of the polycyclic aromatic hydrocarbons studied here.

The goal of this project is to elucidate the spectroscopic properties and reaction dynamics of PAH radicals by a combination of theoretical and experimental techniques. We employ two approaches toward the goal—on one hand, we attempt to characterize a variety of properties and reactions of individual PAH ions thoroughly with an assortment of experimental and theoretical techniques; on the other hand, we employ a single experimental or theoretical technique with wide applicability and a high throughput to study a large

number of PAH ions at once. The greatest challenge from the viewpoint of computation is the development of a theoretical tool that is efficient and accurate for sizable open-shell species that are notoriously difficult for electronic structure calculations.

Previously, we have shown that time-dependent density functional theory (TDDFT) performed remarkably well for the interpretation of the spectroscopic properties of some PAH radicals. In Fiscal Year 2002, we implemented a TDDFT method in NWChem for execution on massively parallel supercomputers. In Fiscal Year 2003, we performed TDDFT calculations for 51 radical cations and seven radical anions of PAH (Figure 1) and presented a uniform, comprehensive interpretation of the spectroscopic data in one place (Hirata et al. 2003a). We have shown that TDDFT is indeed capable of predicting the transition energies to the low-lying excited states of PAH ions within 0.3 eV on average. This accuracy is hardly affected by the sizes of PAH ions, the types of transitions, the types of orbitals involved, or other perturbations. We have also addressed the well-known weakness of TDDFT in dealing with Rydberg excited states and have developed a correction scheme that overcomes such a deficiency (Hirata et al. 2003b).

Concurrently, we combined various experimental techniques ranging from matrix-isolation Fourier transform infrared and ultraviolet-visible light spectroscopies and Fourier transform ion cyclotron resonance mass spectroscopy along with TDDFT to expound upon the structures and reaction of a PAH called 2,3-benzofluorene and its derivatives in great detail (Banisaukas et al. 2004). Apart from the spectral assignment and structural determination made by theory and experiment, the study revealed a fascinating tendency of benzofluorene (shared by other PAHs also) to lose hydrogen and acetylene units successively and eventually become pure carbon clusters. The mechanism of this hydrogen loss process was elaborated by theory and mass spectroscopy, which we believe to have significant implications on the fate of PAHs in interstellar media and in hydrocarbon combustion processes.

This research was performed in part using EMSL's Molecular Science Computing Facility.

References

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- Hirata S, CG Zhan, E Apra, TL Windus, and DA Dixon. 2003b. "A New, Self-Contained Asymptotic Correction Scheme to Exchange-Correlation Potentials for Time-Dependent Density Functional Theory." *Journal of Physical Chemistry A* 107(47):10154-10158.

Seasonal Coupled Meteorology-Chemistry Simulations for the Great Lakes Region

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In addition to the effect of the ozone on human health, it is well known that high surface ozone concentrations can adversely affect many types of vegetation.

The PNNL Eulerian Gas and Aerosol Scalable Unified System (PEGASUS) was used to determine ozone exposure over the Great Lakes region for two time periods: between May and September 1999 and May and September 2001 (Figure 2). PEGASUS was also used to examine the effect of future

anthropogenic emission projections on ozone exposure. These two time periods were selected because the summers of 1999 and 2001 had higher- and lower-than-normal ozone levels over the Great Lakes region, respectively. The modeling system was run in a nested grid configuration, with an outer grid that encompassed eastern North America with a horizontal grid spacing of 36 kilometers and an inner grid over the Great Lakes region with a horizontal grid spacing of 12 kilometers. The number of nodes used on the inner and outer grids was 89 x 89 x 50 and 125 x 92 x 50, respectively. The meteorological driver for PEGASUS was run first to generate the synoptic, mesoscale, and boundary layer atmospheric conditions between May and September 1999 and 2001. The atmospheric conditions at hourly intervals were used to drive the gas-phase chemistry in PEGASUS along with time-varying background lateral boundary conditions for ozone and mobile, area, and point-source emissions of ozone precursors. About 55,000 node hours were required to run the modeling system for the two time periods, and an additional 7,000 node hours were needed for emission projection simulations.

The predicted spatial and temporal variations in ozone concentrations over the Great Lakes region were often consistent with measurements obtained from the U.S. Environmental

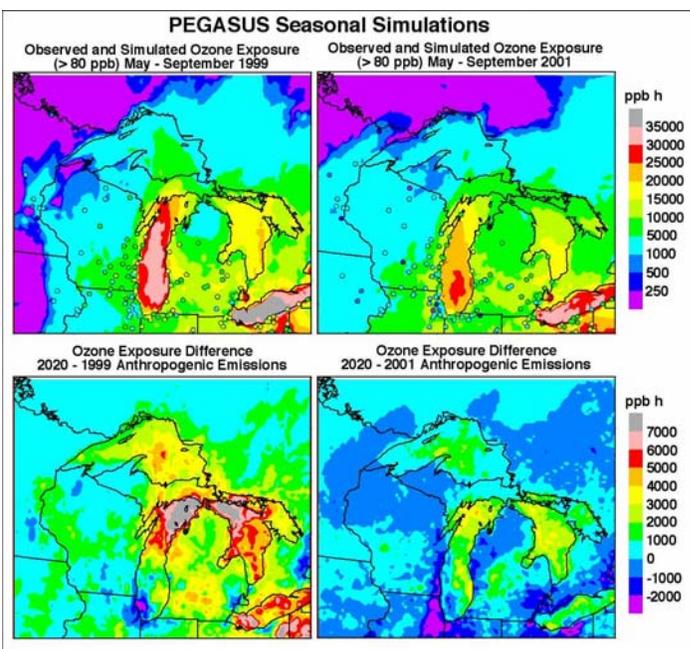


Figure 2. PEGASUS seasonal simulations.

Protection Agency's monitoring stations; however, uncertainties in the emissions estimates and predicted cloudiness likely contributed to model errors at specific times and places. The model also captured the overall month-to-month variability. Ozone exposure, determined as the sum of the hourly ozone concentrations higher than 80 parts per billion (ppb), over the two summer periods is shown in Figure 2. Ozone levels greater than 80 ppb impact human health, while ozone levels greater than 60 ppb have been shown to be detrimental to the health of many types of vegetation. The simulated ozone exposure was found to be higher during Summer 1999 than during Summer 2001, consistent with the measurements in most locations. The largest differences between observed and simulated ozone exposure occurred south of Lake Erie.

An advantage of this model is that it predicts ozone exposure in remote regions where no measurements exist. A fraction of the predicted ozone originating from large urban and industrial sources was transported to the northeast into Canada, impacting the remote forested regions surrounding the Great Lakes. The two simulations were repeated with anthropogenic emission projections for the year 2020 to estimate how ozone exposure will change, given the same meteorological conditions. Figure 2 indicates that the meteorological conditions during Summer 1999 led to lower ozone concentrations in the immediate vicinity of large metropolitan areas, while higher concentrations were produced downwind in remote locations along the shores of the Great Lakes. The meteorological conditions during 2001 resulted in lower increases in ozone given the same emission projections.

This research was supported by the U.S. Department of Agriculture Forest Service and DOE's Atmospheric Sciences Program. Development of PEGASUS was supported by the PNNL Laboratory-Directed Research and Development program. This research was performed in part using EMSL's Molecular Science Computing Facility.

Structure and DNA-Binding Sites of the SWI1 ARID Suggest Determinants for Sequence-Specific DNA Recognition

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The AT-Rich Interaction Domain (ARID) is a homologous family of DNA-binding domains that occur in DNA binding proteins from a wide variety of species, including yeast, nematodes, insects, mammals, and plants. SWI1, a member of the SWI/SNF protein complex that is involved in chromatin remodeling during transcription, contains the ARID motif. The ARID domain of human SWI1 (also known as p270) does not select for a specific DNA sequence from a random sequence pool. The lack of sequence specificity shown by the SWI1 ARID domain stands in contrast to the other characterized ARID domains, which recognize specific AT-rich sequences. Thus, we have solved the three-dimensional structure of human SWI1 ARID using solution nuclear magnetic resonance (NMR) methods. In addition, we have characterized non-specific DNA binding by the SWI1 ARID domain.

Results from this study indicate that a flexible, long internal loop in the ARID motif is likely to be important for sequence-specific DNA recognition (Figure 3). The structure of the human SWI1 ARID domain also represents a distinct structural subfamily. Studies of ARID indicate that the boundary of the DNA binding structural and functional

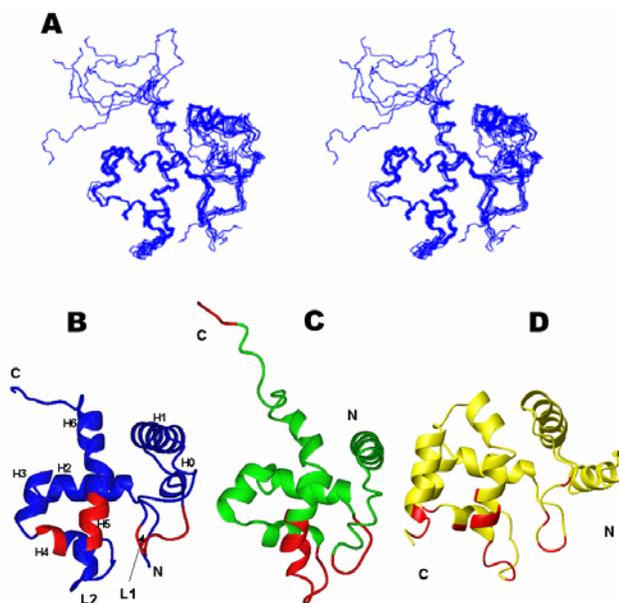


Figure 3. (A) Stereo view of the superposition of a family of 7 structures of the human SWI1 ARID domain. The superposition was obtained by minimizing the root-mean square deviation of backbone heavy atoms in helical regions. (B) The ribbon diagram of the average structure of the SWI1 ARID domain. Helices H0-H6 and the two internal loops are indicated in the figure. (C) The ribbon diagram of the Mrf-2 ARID domain is shown in approximately the same orientation as the SWI1 ARID shown in (B). (D) The ribbon diagram of the Dri ARID domain is shown in approximately the same orientation as the SWI1 ARID shown in (B). The segments involved in DNA binding as indicated by chemical shift perturbation in the Mrf-2 and SWI1 are indicated in red in (B) and (C). The residues involved in DNA binding as shown by the NMR structure of the Dri-DNA complex are indicated in red in (D)

domains can extend beyond the sequence homologous region in a homologous family of proteins. Structural studies of homologous domains such as the ARID family of DNA-binding domains should provide information to better predict the boundary of structural and functional domains in structural genomic studies.

The use of EMSL NMR spectrometers was very helpful in collecting part of the data used to determine the human SWI1 structure. We obtained a ^{13}C -separated NOESY spectrum on EMSL's 600-MHz Varian Inova NMR spectrometer that provided the input peak list for the final structure determination in ARID.

Helium Diffusion through H_2O and D_2O Amorphous Ice: The First Observation of a Lattice Inverse Isotope Effect

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Isotopic substitution has long been an invaluable tool in the experimentalist's arsenal for determining the details of a chemical reaction or diffusion mechanism. In general, if a heavier isotope is substituted for an atom directly involved in a process, the rate for that process is usually slower. For example, in a reaction that involves the breaking of a bond containing a hydrogen atom, the substitution of deuterium will normally result in a decrease in the reaction rate. Thus, through a series of selective isotopic substitutions, one can learn about the microscopic details of a chemical reaction. The decrease in the rate is the result of a lower zero-point energy in the reactant well of the heavier isotope. A lowering of the zero-point energy means a larger energy barrier to reach the transition state and thus a lower rate.

Recently, researchers found that the diffusion rate of helium through amorphous solid water (ASW) is strongly dependent on the isotopic composition of the ASW lattice (Figure 4).

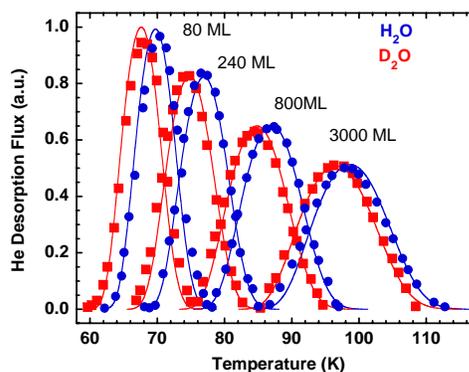


Figure 4. The temperature-programmed desorption (TPD) of helium-implanted ASW (H_2O (circles) and D_2O (squares)) capped with 80, 240, 800, and 2400 milliliters of ASW. The lines through the data are Arrhenius fits using a kinetic hopping model. The data clearly show that helium diffuses more rapidly through D_2O than H_2O .

Further, the lattice isotope effect is the “inverse” of a normal isotope effect, in that diffusion is faster in the heavier (D_2O) isotope lattice. This is the first observation of an isotope effect for diffusion in a solid where the isotopic mass change occurs in the nominally static lattice. The explanation for this inverse isotope effect comes from transition state theory used to calculate the diffusion rate of helium between the ice-like cages. While the helium/ D_2O system lattice does have a lower zero-point energy in the reactant well (helium in an ice-like cage), there is a greater lowering of the zero-point energy at the transition state (helium in a hexagonal water ring), and the net result is an overall lower barrier for helium diffusion in D_2O than in H_2O . This effect, termed a “tight” transition state, is well known for the inverse primary isotope effect observed in hydrogen/deuterium diffusion in palladium and in crystalline ice (Figure 5).

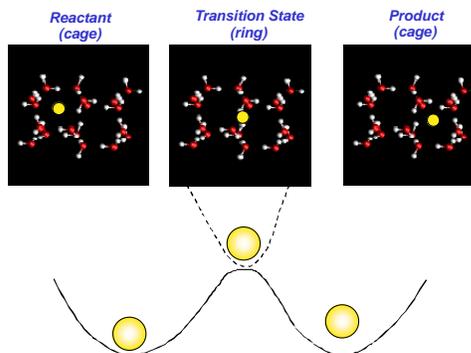


Figure 5. Helium diffusion model. Initially the helium atom is trapped in a water cage. In order to diffuse, it must overcome an energetic barrier (transition state). In this model, the transition state is a hexagonal water ring. After passing through the transition state, the helium atom drops down into the adjacent water cage. The lattice inverse isotope effect observed for helium diffusion in H_2O and D_2O is the result of a “tight” transition state.

In both of these cases, the isotope effect is due to changes in the mass of the diffusing species. In the present case, the isotope effect arises predominantly from vibrational zero-point energy differences associated with the frustrated rotational modes of the H_2O (D_2O) molecules comprising the water lattice. The magnitude of the secondary isotope effect is a sensitive probe of angular anisotropies in the helium–water interaction potential, and the experimental data provide an excellent test of the accuracy of the water/water and helium/water potentials.

High-Pressure Fluorescence and Optical Imaging of Anthracene Single Crystals—The Effect of Nonhydrostaticity

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The broad objective of this research is to examine the origin and nature of electronically accessible structural defects in compressed anthracene single crystals. Specifically, we want to understand the role of nonhydrostatic stresses in formation and modification of structural defects. To pursue this objective, we complemented our previous studies with measurements of fluorescence decay using EMSL resources.

We performed four sets of fluorescence decay measurements of anthracene single crystals under high pressures in a diamond anvil cell, employing either 360-nanometer or 532-nanometer excitation lines from a mode-locked Nd:YAG laser. A time-correlated single-photon counting system with a multichannel-plate photomultiplier tube was used for detecting the fluorescence decays. We obtained pressure dependence of fluorescence decays under hydrostatic and nonhydrostatic conditions using excitation within the singlet (360-nanometer) and triplet (532-nanometer) states absorption. In hydrostatic conditions, a gradual increase of nonradiative rates with increasing pressure was observed. However, under nonhydrostatic conditions, the fluorescence decays changed their character, exhibiting an apparent build-up component (Figure 6). The occurrence of the build-up component in the fluorescence decays was correlated with other changes detected in fluorescence spectra and optical images. We propose that the nonhydrostatic stresses generated a range of structural defects in the compressed crystal, with the fluorescence decay measurements helping to determine the nature of the defects.

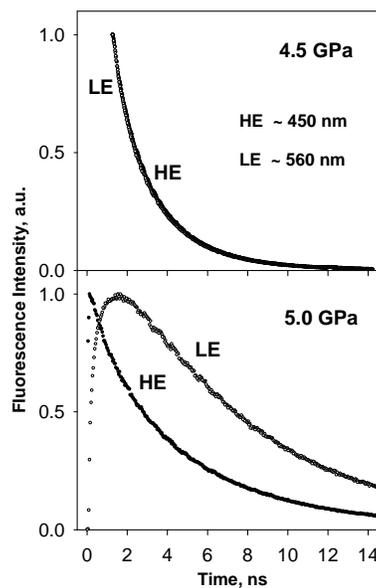


Figure 6. Fluorescence decay curves for the low- (LE) and high-energy (HE) part of the fluorescence spectra at hydrostatic (4.5 GPa) and nonhydrostatic pressures (5.0 GPa).

Proteomic Analysis of a Hepatitis C Virus Cell Model System

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The development of a reproducible model system for the study of hepatitis C virus (HCV) infection will significantly enhance research of host/viral interactions within the cell and provide future direction for modeling the pathogenesis of HCV. Large-scale proteome analysis of the Huh-7.5 HCV replicon model can potentially reveal critical host protein targets as characteristic signals of HCV infection. For this research, offline strong cation exchange liquid chromatographic tryptic peptide separations, prepared from subcellular fractions of Huh-7.5 cells (+) and (-) of the HCV replicon, were used in combination with high-resolution, reversed-phase capillary liquid chromatography (LC) coupled to electrospray ionization-tandem mass spectrometry (MS/MS) analysis. This method resulted in the detection of greater than 25,000 peptide identifications corresponding to more than 4,500 confidently identified proteins using conservative search criteria (Figure 7) and normalized elution time constraint.

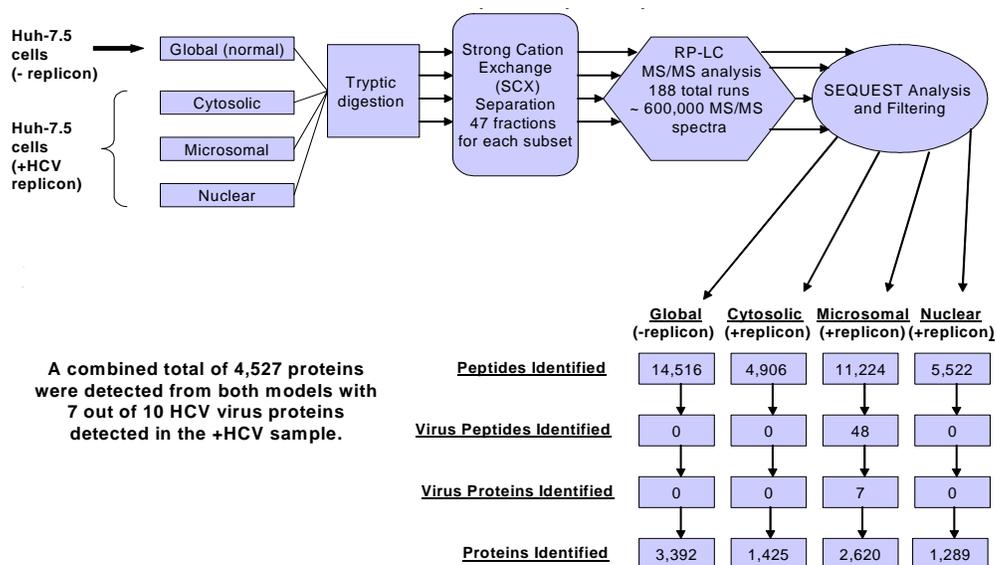


Figure 7. Schematic of Huh-7.5 cells +/- HCV replicon peptide separation and identification.

In addition, seven out of 10 HCV replicon proteins were detected by LC-MS/MS using SEQUEST analysis, with all 48 detected viral peptides corresponding to the seven HCV proteins specifically localized to the microsomal subcellular fraction prepared from the (+) HCV sample. Preliminary determination of differences in cellular protein abundances

between Huh-7.5 cells (+) and (-) of the HCV replicon has revealed either the up- or down-regulation of important cellular pathways in response to HCV infection. These initial results represent a significant mass tag database that can be applied to the Fourier transform ion cyclotron resonance accurate mass and time (AMT) tag proteomic characterization of liver tissue and provide a foundation for future HCV infection proteomic analyses.

Hydrocarbon Analogues of Boron Clusters—Planarity, Aromaticity, and Antiaromaticity

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An interesting feature of elemental boron and boron compounds is the occurrence of highly symmetric icosahedral clusters. The rich chemistry of boron is also dominated by three-dimensional cage structures. Despite boron's proximity to carbon in the periodic table, elemental boron clusters have been scarcely studied experimentally and their structures and chemical bonding have not been fully elucidated. In Zhai et al. 2003, it is shown that small boron clusters prefer planar structures and exhibit aromaticity and antiaromaticity according to the Hückel rules, akin to planar hydrocarbons (Figure 8). Aromatic boron clusters possess more circular shapes, whereas antiaromatic boron clusters are elongated, analogous to structural distortions of antiaromatic hydrocarbons. The planar boron clusters are thus the only series of molecules other than hydrocarbons to exhibit size-dependent aromatic and antiaromatic behavior and represent a new dimension of boron chemistry.



Figure 8. Lai-Sheng Wang (from left), Kiran, Zhai, and Li have provided additional experimental and theoretical evidence for the existence and properties of planar all-boron clusters, ranging from B₃ to B₁₅.

This research was performed in part using EMSL's Molecular Science Computing Facility.

Reference

Zhai HJ, B Kiran, J Li, and LS Wang. 2003. "Hydrocarbon Analogues of Boron Clusters—Planarity, Aromaticity and Antiaromaticity." *Nature Materials* 2(12):827–833.

Influence of GaN Template Layer Strain on the Performance of InGaN/GaN Multilayer Quantum Well Light Emitting Diodes

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Group-III nitrides have become extremely important in device applications over the last decade. High-brightness light emitting diodes (LEDs) and high-power laser diodes based on these materials are already commercially available. However, due to excess dissociation pressure at the high temperatures necessary for crystal growth, Group-III nitrides cannot be fabricated economically in bulk single-crystal form. As such, these materials must be deposited heteroepitaxially on a foreign substrate. For example, InGaN/GaN multilayer quantum well (MQW) structures are typically grown atop a GaN template layer deposited on a sapphire substrate. However, GaN has large lattice and thermal expansion coefficient mismatches with sapphire, approximately 32 percent and 56 percent, respectively. The resulting strain and defect formation in the GaN template can affect the properties of the overlying MQW structure.

In this study, we examined the effects of template strain on the performance of two seven-period InGaN/GaN MQW LEDs grown by metallorganic chemical vapor deposition. Except for the thickness of the GaN template layers (5 μm and 15 μm , respectively), the deposition parameters were identical. Figure 9 shows that the electroluminescence emission of the device grown atop the 15 μm template was red-shifted by ~ 132 meV. An overlay plot of the triple-axis X-ray diffraction (TAXRD) rocking curves for both LEDs is shown in Figure 10. The many well-resolved satellite peaks showed that these were high-quality films, while the position of the GaN (002) peak indicated that the perpendicular strain was +0.04 percent in the 5- μm template and -0.002 percent in the 15- μm template. Although not illustrated here, the position of the asymmetric GaN (105) peak for these films indicated that the parallel strain was -0.10 percent in the 5- μm template and +0.009 percent in the 15- μm

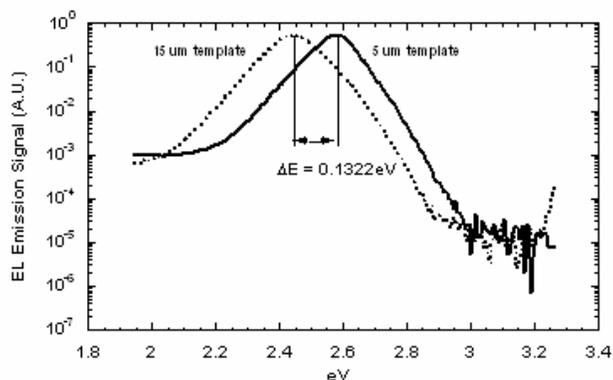


Figure 9. Electroluminescence emission for InGaN/GaN MQW devices grown simultaneously on 5- μm and 15- μm GaN templates. The output of the device on the 15- μm template is red-shifted by ~ 132 meV.

template. These results revealed there was less residual strain in the thicker template. Cross-section transmission electron microscopy images of both devices are shown in Figure 11.

These images verified the thickness of the template layers. In addition, the edge dislocation density was $0.4 \times 10^8 \text{ cm}^{-2}$ in the 5- μm template and $1.9 \times 10^8 \text{ cm}^{-2}$ in the 15- μm template. Note that the higher dislocation density in the thicker template was consistent with the strain relaxation observed by TAXRD. Depth profiling by dynamic secondary ion mass spectroscopy was also performed to obtain the indium concentration in the active region of these devices. On a relative scale, the average indium concentration was ~11 percent higher for the device grown on the 15- μm template.

This difference in indium concentration was attributed to strain-induced thermodynamic effects that influenced the MQW growth and ultimately caused the red-shift illustrated in Figure 9. These results showed the importance of template strain in the design and fabrication of InGaN/GaN MQW LEDs.

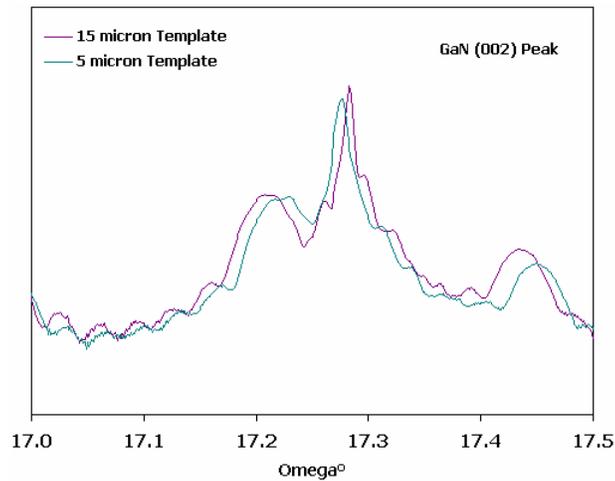


Figure 10. Expanded scale overlay plot of the TAXRD rocking curves for both devices.

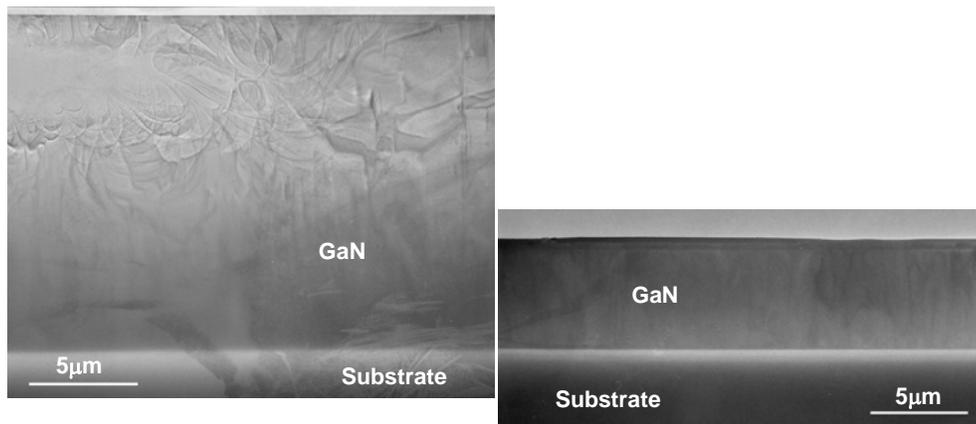


Figure 11. Cross-section transmission electron microscopy images of both devices showing the differences in template layer thickness and dislocation density. The edge dislocation density was $0.4 \times 10^8 \text{ cm}^{-2}$ in the 5- μm template and $1.9 \times 10^8 \text{ cm}^{-2}$ in the 15- μm template.

Dissolution and Growth of $(10\bar{1}4)$ Calcite in Flowing Water: Estimation of Back Reaction Rates via Kinetic Monte Carlo Simulations

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Although calcite is an important mineral for many processes, there have been relatively few simulations of its growth and dissolution behavior. Such simulations are complicated by the multitude of defect types and by the asymmetry of the crystal. In a recent paper (Williford et al. 2004), work combining a kinetic Monte Carlo model involving a modified cubic crystal structure and a Blasius liquid boundary layer was performed to simulate the simultaneous growth and dissolution reactions on the calcite cleavage surface in flowing water. The model was developed as part of a DOE

Office of Basic Energy Sciences Geosciences program to help understand the impact of solution flow on measurements made of pit growth using EMSL's atomic force microscope. The activation energies of the back reaction (growth) were determined from those of the forward reaction (dissolution) by obtaining agreement with cleavage-step morphologies and step-dissolution velocities over a range of flow rates measured using the atomic force microscope. Because the model includes the elemental reaction steps, information about the occurrence of specific steps influencing an overall reaction rate can be estimated. The kinetics of dissolution and growth were found to be dominated by diffusion events on the solid/liquid interface and in the liquid, as expected. One of the experimental observations involves changes in the shape of steps as solution flow changes. The differences between a relatively smooth dissolution step at rapid solution flow and a rougher step for slower solution flow can be seen in Figure 12. The relative magnitude of the desorption and adsorption activation energies were consistent with experimental data, entropic arguments, and crystal roughening theories. Because all of the boundary layer parameters cannot be determined from first principles, there is one adjustable parameter involved in fitting the data. However, quantitative agreement with measured step velocities is best when the boundary layer parameters were given physically reasonable values as shown in Figure 13.

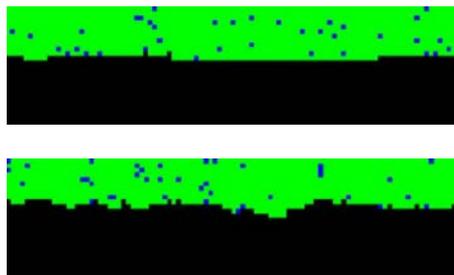


Figure 12. Example of steady-state step face geometry calculated by the Kinetic Monte Carlo method at high flow rate (top) and at low flow rate (bottom).

In addition to those mentioned above, the results of the simulations exhibit several interesting features. The simulated step morphologies are in good qualitative agreement with scanning probe microscope images over the full range of flow rates. Events at the step face are dominated by surface diffusion (~70 percent), as expected. Desorption and adsorption account for about ~15 percent each. The approach to equilibrium is rapid because of the small size of the liquid region in the model. A larger liquid region simply required more cycles to reach equilibrium, but results were

within the scatter inherent in the Kinetic Monte Carlo method. Activation energies for adsorption (growth) were found to be less than those for desorption (dissolution). This is consistent with crystal roughening theories and with experiments on bulk calcite. Several authors have explored the phenomenon of 'kinetic asymmetry' associated with crystal roughening theories. For smooth surfaces, it is found that growth rates are generally faster than dissolution rates, in agreement with rate constants computed from the present simulations. The situation is reversed for rough surfaces, especially at the corners of growth islands. The Blasius boundary layer approximation appears adequate for simulation of calcite dissolution and growth under flowing fluid conditions in the atomic force microscope wet cell. The flow constant corresponds to a boundary layer development length of 7.8 Angstroms. This is physically reasonable because it indicates that the boundary layer is developing within a few lattice constants for the given flow conditions. It is also in agreement with the previously reported 5.3-Angstrom-thick 'organized water layer' on calcite surfaces. Thus, the model appears self-consistent.

Reference

Williford RE, DR Baer, JE Amonette, and AS Lea. 2004. "Dissolution and Growth of $(10\bar{1}4)$ Calcite in Flowing Water: Estimation of Back Reaction Rates via Kinetic Monte Carlo Simulations." *Journal of Crystal Growth* 262:503-518.

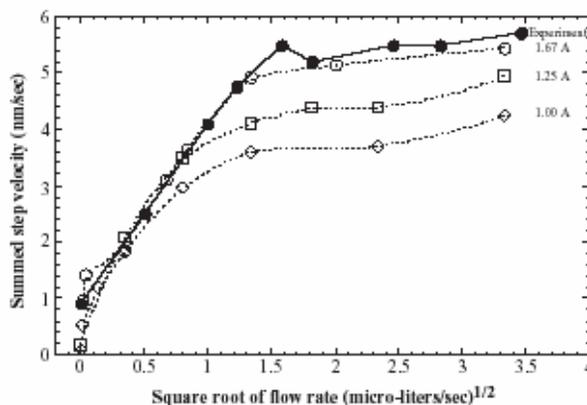


Figure 13. Sum of step velocities versus the square root of the fluid flow rate. Numbers indicate multipliers for the entropic prefactors (AD and AA).

Synthesis and Characterization of Dendrimer-Derived Monometallic Ru and Bimetallic Pt-Ru Catalysts

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Supported catalysts play a central role in industrial chemical processes, as well as in pollution abatement. In such catalysts, the average particle size and particle size distribution of the supported nanoparticles are often critical for controlling catalytic performance (i.e., activity and/or selectivity). Recently, dendrimers were successfully used to template and stabilize metal

nanoparticles in solution. Dendrimers (Figure 14) are hyperbranched polymers with a specific molecular structure and are particularly well-suited for hosting metals for the following reasons: (1) the dendrimer templates themselves are of fairly uniform composition and structure, and therefore they can yield well-defined nanoparticles reproducibly; (2) the nanoparticles are stabilized by encapsulation within the dendrimer, and therefore they do not agglomerate; and (3) the terminal groups of the dendrimer periphery can be tailored to control solubility of the hybrid nanocomposites and therefore, can be used as handles for facilitating linking to surfaces and other polymers.

Hydroxyl-terminated polyamidoamine (PAMAM) dendrimers include interior tertiary amine groups that can chelate metal ions. Following complexation of the metal ions with the dendrimer amine groups, a reduction step can yield to dendrimer-encapsulated metal nanoparticles. Deposition of the metal-dendrimer nanocomposites onto an oxide support and removal of the dendrimer "shell" by thermal treatment can lead to supported catalysts with a very narrow particle size distribution.

Results of previous studies have indicated that Pt⁴⁺ ions (from a H₂PtCl₆ precursor) can complex with a PAMAM dendrimer. Ultraviolet-visible spectroscopic results indicate that Ru³⁺ ions (from a RuCl₃ precursor) are also capable of complexing with the dendrimer structure. In a subsequent reduction step, the Ru³⁺ ions yield finely dispersed ruthenium nanoparticles with a narrow particle size distribution. These dendrimer-stabilized nanoparticles were then deposited onto an alumina support and thermally activated to remove the dendrimer "shell." Despite some mild sintering observed during this activation process (Figures 15a and 15b), high-resolution transmission electron microscopy (HRTEM)

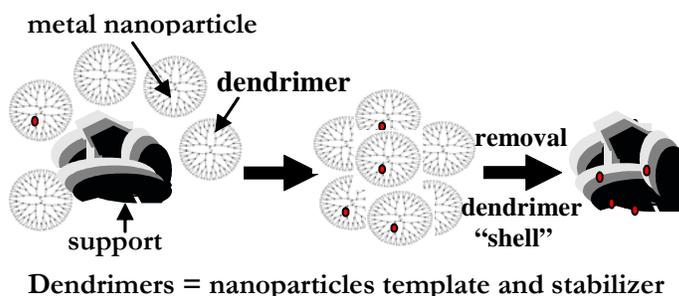


Figure 14. Synthesis of well-dispersed oxide supported nanoparticles using a dendrimer precursor.

measurements indicated that the resulting ruthenium/ Al_2O_3 catalyst has a smaller than average metal particle size and a narrower particle size distribution than a similar catalyst prepared by a traditional wet impregnation from the same RuCl_3 precursor (Figures 15b and 15c).

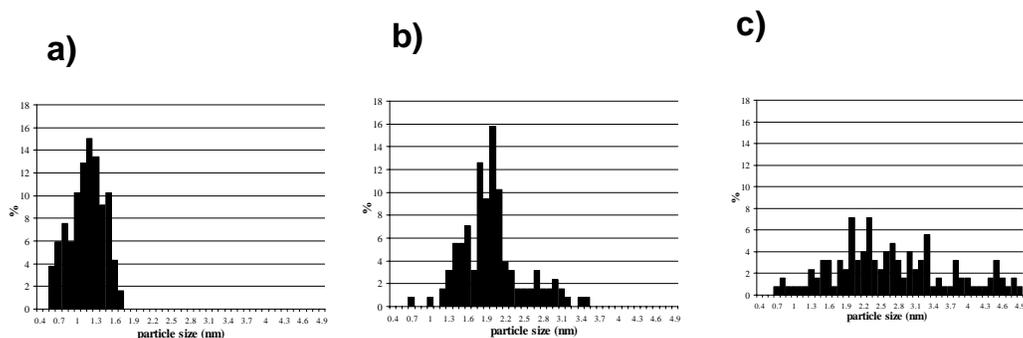


Figure 15. Metal particle size distributions of (a) ruthenium-G4OH PAMAM nanocomposites in solution; (b) a 1%wt $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst prepared from a ruthenium dendrimer precursor and reduced for two hours at 300°C ; and (c) a 1%wt ruthenium/ Al_2O_3 catalyst prepared directly from a RuCl_3 precursor and reduced for two hours at 300°C .

In the course of preparing supported bimetallic catalysts, the main difficulty is to create an intimate contact between the two metals in order to obtain a synergistic catalytic effect. Classical co-impregnation or successive impregnations often prove to be unsatisfactory, since metal segregation is frequently observed. We have investigated the synthesis of bimetallic platinum-ruthenium catalysts via the dendrimer method following either co-complexation/co-reduction or sequential complexation/reduction protocols. Energy dispersive X-ray microanalysis of supported platinum-ruthenium/ Al_2O_3 catalysts thus obtained reveals that truly bimetallic particles are formed in both cases. Sequential complexation can result in selective surface enrichment of one of the two metals with direct consequences on the catalytic properties of the resulting materials. In fact, despite their similar particle size distributions (obtained via HRTEM measurement), X-ray photon spectrometry and Fourier transform infrared studies of adsorption CO reveal that the structure and surface properties of these platinum-ruthenium catalysts are strongly affected by the preparation protocol.

Raman Under Nitrogen: The High-Resolution Raman Spectroscopy of Crystalline Uranocene, Thorocene, and Ferrocene

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The utility of recording Raman spectroscopy under liquid nitrogen, a technique called Raman under nitrogen (RUN), was demonstrated for ferrocene, uranocene, and thorocene for the first time. Using RUN, low-temperature (liquid nitrogen-cooled) Raman spectra for these compounds exhibited higher resolution than previous studies, and new vibrational features were reported. A broad, polarizable band centered at ~ 460 cm^{-1} was greatly enhanced relative to the vibrational Raman transitions with excitations from the krypton ion laser, which is indicative of an electronic resonance

Raman process. The electronic resonance Raman band was observed to split into three distinct bands at 450, 461, and 474 cm^{-1} with 6764-Å excitation. By using relativistic density functional theory, the vibrational spectra of the actinocenes were assigned and interpreted. It is shown that the fine structure of the electronic Raman transition is due to the spin-orbit splitting of the ground and first excited state (Figure 16). This work shows that in combination with theoretical modeling, the RUN technique can provide high-resolution spectroscopic information on the electronic structures of actinide complexes.

This research was performed in part using EMSL's Molecular Science Computing Facility.

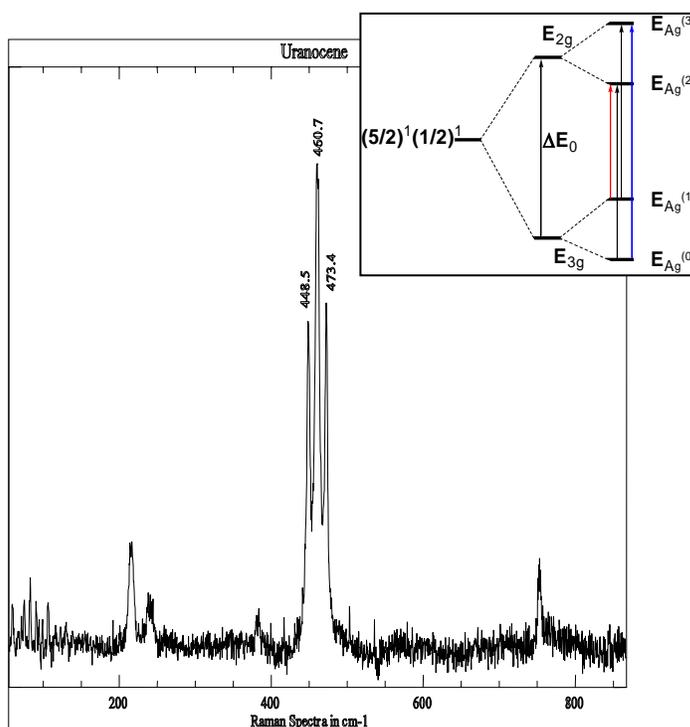


Figure 16. Observed Raman spectra and theoretical interpretation of the splitting of the electronic transition.

On the Electronic Structure of Molecular UO_2 in the Presence of Ar Atoms: Evidence for Direct U-Ar Bonding

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(c) University of Virginia, Charlottesville, Virginia

(d) Universite Paul Sabatier, Toulouse, France

Jun Li et al. (2002) previously discovered the existence of uranium-argon bonding in $\text{CUO}(\text{Ar})_n$ complexes. In the current work, theoretical calculations via scalar-relativistic density functional theory and ab initio CCSD(T) methodologies are used to explore the possibility of direct interactions between molecular UO_2 and argon atoms. The ${}^3\text{H}_g$ electronic state of UO_2 , which is an excited state of the isolated UO_2 molecule, exhibits significant bonding to argon in the model complexes $\text{UO}_2(\text{Ar})$ and $\text{UO}_2(\text{Ar})_5$. The calculated vibrational frequencies of ground-state ${}^3\Phi_u$ UO_2 , and

$\text{UO}_2(\text{Ar})_5$ with an (f)1(f)1 electron configuration agree well with the observed frequencies of UO_2 in solid neon and solid argon, respectively. The results strongly suggest that the ground electron configuration of UO_2 changes from 5f17s1 to 5f2 when the matrix host is changed from neon to argon (Figure 17). This work thus provides strong evidence that there is direct uranium-argon bonding in low-temperature conditions and further supports the idea of ground-state reversal of the actinide complexes upon actinide-noble gas bonding.

This research was performed in part using EMSL's Molecular Science Computing Facility.

Reference

Li J, BE Bursten, B Liang, and L Andrews. 2002. "Noble Gas-Actinide Compounds: Complexation of the CUO Molecule by Ar, Kr, and Xe Atoms in Noble-Gas Matrices." *Science* 295(5563):2242-2245.

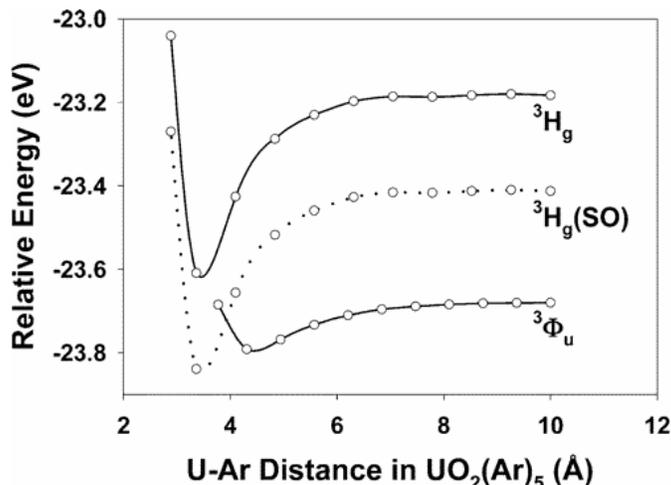


Figure 17. Calculated linear-transit potential energy curves for D_{5h} $\text{UO}_2(\text{Ar})_5$ for the ${}^3\Phi_u$ and ${}^3\text{H}_g$ electronic states of UO_2 . The dotted line represents a lowering of the curve for the ${}^3\text{H}_g$ state by a constant 0.23 eV to account for differential spin-orbit stabilization of the ${}^3\text{H}_g$ state.

NWPerf

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(b) Pacific Northwest National Laboratory, Richland, Washington

We present NWPerf, a new system for analyzing fine granularity performance metric data on large-scale supercomputing clusters. This tool is able to measure application efficiency on a system-wide basis from both a global system perspective as well as provide a detailed view of individual applications. NWPerf provides these capabilities while minimizing the impact on the performance of user applications. The system may be used to detect and eliminate performance problems in an application, resulting in improved performance by up to several thousand percent. The NWPerf architecture has proved to be a stable and scalable platform for gathering performance data on a large 1954-CPU production Linux cluster at the Pacific Northwest National Laboratory in Richland, Washington.

Computing jobs are showing a general trend towards improved performance on EMSL's MPP2 supercomputer, as shown by the percentage of peak flops from October 2003 through March 2004 (Figure 18).

MPP2 statistics for peak (flops) show a correlation of NWPerf performance to job size. We see a spot at about the 256-node size where the mean and median deviate (Figure 19). This jump in performance over the general trend is directly attributable to two Computational Grand Challenge users running larger jobs.

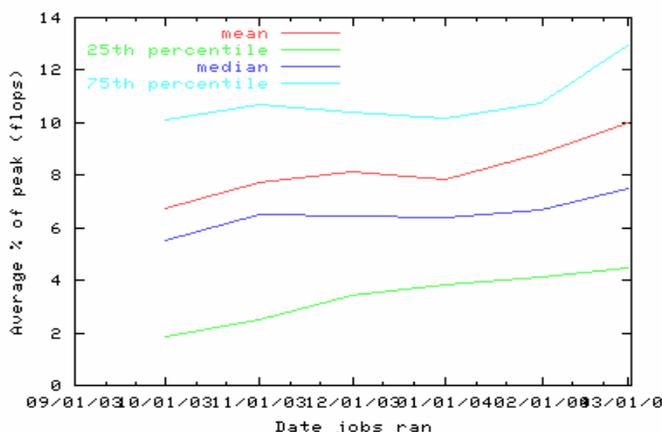


Figure 18. Trend toward improved performance on EMSL's MPP2 supercomputer, following use of NWPerf.

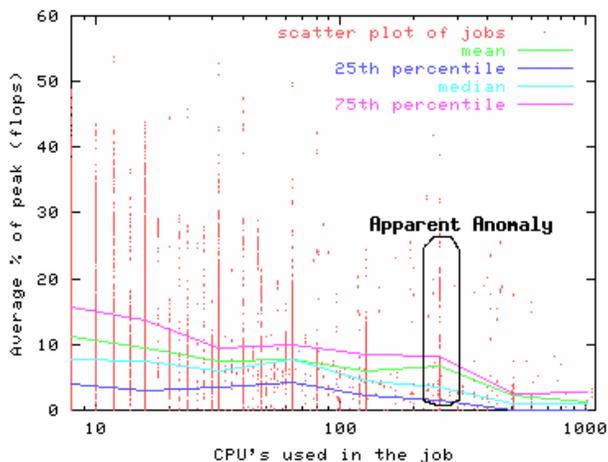


Figure 19. Job size has a direct correlation to performance of NWPerf.

Finally, we used NWPerf to search for a problem in a mass spectrometry analysis code that had a performance problem; use of NWPerf improved the code's performance by about 400-fold. These resulting data were then used to search for other jobs with similar characteristics and assist the associated users with resolving their problem. As a result, one biogeochemistry code reported improvements of over 50 percent by changing a few compiler flags as a result of our feedback.

Confocal Microscope with FPGA Processing

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

(b) Pacific Northwest National Laboratory, Richland, Washington

EMSL's high-speed confocal microscope can simultaneously acquire two color images at speeds up to 30 frames per second, providing the capability to perform near-real-time fluorescent resonance energy transfer (FRET) and ratiometric analysis of confocal images. Confocal capabilities are necessary for three-dimension reconstruction and correlation of image slices with identified signaling and propagation chemistry, using observation of the fluorescence originating from spatially localized portions of cells. Such information is important not only for addition to the existing knowledge base related to cellular signaling in general, but it also provides primary data to critically test developing spatial models of intercellular signaling.

The high-speed confocal microscope is designed to simultaneously capture output from two intensified charge-coupled diode cameras. Software provided by the EMSL Instrument Development Laboratory controls laser output from the microscope via an eight-channel acoustic-optic tunable filter. This custom software also controls the XY axis of the microscope using a high-resolution Ludl stage, and controls the Z-axis using a PT piezo focus drive. Images from the two cameras are acquired synchronously and merged using a software package developed at PNNL. To maximize the flexibility of the control software, this software package uses a text-based script engine that exposes the functionality of all hardware components of the system, allowing the operating scientist to build or customize ad hoc experiments.

The fundamental software/hardware infrastructure needed to conduct "real-time FRET" includes two cameras that are matched and aligned to the pixel level so that alternate frames are acquired using alternate excitation wavelengths, and also the ability to capture images from both cameras simultaneously. The capability to match and fuse two images in real time is being developed by the Instrument Development Laboratory using a field-programmable gate array as a reconfigurable processor. Additional manipulations include averaging of multiple images, co-adding images to create 16-bit pseudo-color images, and achieving a ratio of different images, with a correct registration of pixels.

Control System for an Inexpensive and Configurable Ion Trap Mass Spectrometer

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

(b) Pacific Northwest National Laboratory, Richland, Washington

This project involved the development of an ion trap mass spectrometer that is both inexpensive and flexible, opening up the application of ion trap technology to a number of research areas. The primary thrust was to develop a basic hardware and software platform for ion trap mass spectrometry (ITMS) that will allow construction and deployment of systems with capabilities tailored to specific needs of a variety of scientific applications, with emphasis on use of chemical ionization techniques to address the need for highly sensitive and specific measurements as well as analytical needs dictated by research areas such as atmospheric chemistry, catalysis, materials science, biology, and inhalation toxicology.

This ITMS platform can be used to develop and deploy systems for critical applications such as chemical weapons detection and nuclear proliferation monitoring. Although commercial ITMS systems are available, their hardware and software are tailored for specific needs and are not easily modified. Additionally, the cost of commercial systems (\$20K for the new ITMS platform versus \$60K to \$200K for a commercial system) places them beyond the means of many academic researchers, particularly at smaller institutions. Thus, we have created a platform using inexpensive, commercially available computers, data acquisition systems, and control equipment combined with open source software for instrument control, data acquisition, and analysis. As such, the software can be readily tailored to specific applications, in contrast to commercial ITMS systems.

The hardware and software developed as part of this project enhance and extend the capabilities of two instruments used within EMSL: the proton transfer ion trap mass spectrometer and the laser desorption ion trap mass spectrometer (LD-ITMS). The control system includes some components specific to the LD-ITMS system for the analysis of single biological and non-biological particles, as an illustration of one application. The remainder of the system can be used by a wide range of ITMS applications.

The control and acquisition hardware consists of four National Instruments PCI boards that provide the signal generation, timing, and data acquisition for the system. An optional component of the system is a field-programmable gate array-based particle discriminator. Developed in the Instrument Development Laboratory, this particle discriminator is used to trigger an ablation laser as a particle passes through its beam. The control software was written in Visual Basic 6.0 to take advantage of its Rapid Application Development environment and straightforward integration with the control hardware.

The system was showcased at National Instruments NIWeek 2003 conference, where it was a finalist in the Lab Automation/ R&D category of the paper contest, and featured on the cover of *Scientific Computing and Instrumentation Magazine*, April 2004.

Novel Cooling Technology

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

Researchers from EMSL, the Pacific Northwest National Laboratory (PNNL), and Isothermal Systems Research are collaborating on the design and evaluation of a novel cooling technology—SprayCool (patented by the latter company)—on a portion of PNNL's supercomputer. This evaluation will be conducted to measure improvements in computational speed and system reliability through this improved equipment cooling.

Heat generation is one of the most critical limitations in high-performance computing, and electronics in general. Electronic circuits consume power and, hence, generate heat, in direct proportion to their clock speed. With clock speeds now well into the gigahertz range, performance is often limited not by semiconductor technology, but instead by how much heat can be removed. If the heat is not adequately removed, the circuit will be destroyed. This is analogous to an automobile engine that overheats under load and thus must slow down to avoid being permanently damaged. Next-generation microprocessors have potential power dissipation of more than 100 watts, well beyond the capacity of current air cooling technologies. This limitation is resolved by slowing the microprocessor, which in effect reduces its computing capacity, thus impacting the effective computational rate of PNNL's supercomputer.

SprayCool technology addresses this problem by replacing the typical cooling medium (moving air) with a fluorinert (3MTM) liquid that is sprayed directly in a finely atomized stream on the component being cooled. The liquid is vaporized on contact, and the heat of vaporization is supplied by the component, effectively cooling it. The vapor is removed from the cooling apparatus and sent to a heat exchanger outside of the equipment cabinet. The heat exchanger cools the vapor, returning it to liquid form for reuse. The system is completely closed-looped, with none of the cooling liquid vented to the atmosphere. The SprayCool technology can potentially remove 500 times the heat of conventional forced air cooling methods.

Awards and Recognition

Grant to Explore Cooling Methods. The Molecular Science Computing Facility Operations group recently received \$3M to research the application of exotic cooling methods to microprocessors in high-performance computing systems. This research will be performed in partnership with Isothermal Systems Research (ISR), a Spokane-based company that specializes in cooling and environmental isolation (separating the computing equipment from harsh environments). The research will involve comparing ISR's SprayCool™ cooling technology to conventional air cooling in high-performance computing environments.

EMSL User Receives Award. EMSL user Zsuzsanna Balogh, Washington State University, Pullman, Washington, received the outstanding graduate student in geology award. Balogh is working with Tom Dickinson, Washington State University, Pullman, Washington, on the effects of fungal hyphae and other microorganisms from the roots of conifers on the weathering of mineral-grain surfaces in relation to nutrient uptake by the microbial-conifer ecosystem. She is using EMSL scanning electron microscopy and X-ray microanalysis to examine root, fungal, and mineral associations, chemical weathering patterns on mineral surfaces, and mineral identification.

Professional/Community Service

Take Our Daughters and Sons to Work Day. More than a dozen local elementary school students visited the Environmental Spectroscopy and Biogeochemistry Facility's Electron Microscopy Laboratory during "Take Our Daughters and Sons to Work Day" held April 22. The budding scientists received hands-on experience with "real" optical microscopes and observed the large electron microscopes in action. The students agreed that the intricate image of an insect magnified over 30,000 times its size was pretty neat.

Also part of the annual Take Our Daughters and Sons to Work Day activities, EMSL's Jim Alzheimer with the Battelle Robotics Automation Technology Society (BRATS), presented demonstrations of mini sumo robots. This well-attended presentation was aimed at instilling a sense of excitement about science and technology in the participants. A discussion of the rules and basic design of the machines was briefly offered, but the really fun part was watching the robots push and dance around the ring. Organizers received many good ideas from the participants for improvements and completely new concepts. Another demonstration was held earlier in the day, with a web broadcast to students at Seneca Valley High School, Maryland. In addition, EMSL's Eric Choi showed the participants the Temperature INvestigating Mobile AutomatoN—a temperature-mapping robot under development at the Instrument Development Laboratory.

Extended Organizing Committee Meeting. Gordon Anderson, EMSL's Instrument Development Laboratory Technical Group Lead, recently attended the Extended Organizing Committee Meeting to help develop the agenda for the data management workshop to be held in Chicago on May 24 - 26. This data management workshop will be the second DOE Office of Advanced Scientific Computing Research/Mathematical, Information, and Computing Sciences-sponsored meeting designed to identify the challenges posed by data-intensive science supported by the DOE Office of Science. Anderson represented the data management needs of the biology research area. Anderson and Pacific Northwest National Laboratory researchers James Myers, George Chin, Eric Stephan, Deborah Gracio, and Ron Taylor prepared a set of biology workflow diagrams for the May workshop.

WSU EECS Open House and Advisory Council Meeting. Recently, EMSL Instrument Development Laboratory staff members Tom Seim and Eric Choi attended the two-day Washington State University (WSU) Electrical Engineering and Computer Science (EECS) Open House and Advisory Council Meeting. Staff provided advice for future improvements to and development of the university's EECS curriculum, and observed a Programming Language Design class; student teamwork-oriented projects (including EMSL's WSU Temperature INvestigating Mobile AutomatoN project and the PNNL Security Light Control project, both of which have had WSU interaction); and a Sumo Robot competition among WSU Institute of Electrical and Electronics Engineers students, PNNL's Battelle Robotic Automation Technology Society members, Southridge High School students, Mathematics Engineering Science Achievement students, and Pullman High School students. Staff members also attended WSU advisory council meetings where the university presented their vision of the future of their EECS program. Members of industry and PNNL provided much input to WSU, including a suggestion to implement a mentoring program among local companies and WSU.

MSCF Computational Grand Challenges. On April 16, the MSCF received 17 Letters-of-Intent to submit Computational Grand Challenge application proposals. MSCF staff completed an internal technical merit review and provided comments to each of the authors to help them with final proposal submission, due on May 31. Based on the judgment of the internal reviewers, the projects were categorized into one of four EMSL mission areas. Table 1 shows these four areas of research and a summary of the requested computing hours for each. The projected available computing hours for Fiscal Year 2005 is 5,500,000.

Areas of Research	Numbers Submitted	Requested Computing Hours/Year
Chemistry	10	8,050,000
Biology	5	4,600,000
Environmental Science/Subsurface	2	1,500,000
Climate	0	0
Total	17	14,150,00

Table 1. Requested computing time for EMSL Computational Grand Challenges.

Computing Facility Tutorial. On March 24, the Molecular Science Computing Facility's Visualization and User Services group held an onsite tutorial, entitled "MSCF for Dummies 2004." This 2.5-hour tutorial about the facility's MPP2 supercomputer was split into two sessions. The first was geared toward beginner and intermediate users, with topics related to day-to-day use of the supercomputer (e.g., running jobs, available software, commands). The second session focused on expert users and software development (e.g., covering compilers, debuggers, and profiling). Using the latest technology, the tutorial was streamed live onto the web for the first time, allowing offsite EMSL users to participate. About 10 people attended the tutorial onsite, while more than 20 sites (75 people) followed the tutorial via the live stream. The slides and tutorial video are available to the EMSL user community on the [Molecular Science Computing Facility training](#) web page

Major Facility Upgrades

A new picosecond diode-pumped Nd:YAG laser was installed in the Environmental Spectroscopy Laboratory within the Environmental Spectroscopy and Biogeochemistry Facility. The laser provides output of 2 watts of 532-nanometer pulses at a repetition rate of 76 megaHertz and a pulsewidth of 12 picoseconds. The output can be used to synchronously pump a dye laser, providing tunable picosecond pulses in the visible (560 to 760 nanometers) and near-ultraviolet (280 to 380 nanometers) range through second harmonic generation. This laser can be used to measure luminescence lifetimes by coupling with the Hamamatsu streak camera (time resolution ~10 picoseconds) or a time-correlated single-photon counting system (time resolution ~50 picoseconds). Current experiments involve measuring the fluorescence lifetimes of doped, inorganic nanoparticles.

RAID5 and RAID6 Arrays. Due to changes made to the Molecular Science Computing Facility's Linux 2.6 kernel, Software RAID5 and RAID6 arrays greater than two terabytes can now be created. In testing these changes, a six-terabyte array was created using low-cost Serial ATA disk drives, which we believe to be the largest Software Raid5/6 array created under Linux. This will enable low-cost, high volume storage that will enable proteomics and other high storage volume projects.

High-Performance Disk-Based Storage. Battelle, on behalf of Pacific Northwest National Laboratory, anticipates a large increase in storage requirements due to the increased focus on bioinformatics, climate, and high-performance computing. In preparation for this anticipated growth, the Molecular Science Computing Facility is procuring a new \$1M to \$3M high-performance disk-based storage system to be delivered and installed at EMSL in the next 4 to 16 months. This new storage system is expected to provide approximately 200 terabytes of high-performance storage in a single filesystem, usable by hundreds of client systems simultaneously.

News Coverage

David Hoyt in *Laboratory Equipment Magazine*. David Hoyt, Technical Lead of the High-Field Magnetic Resonance Facility, was featured in the March 2004 issue of *Laboratory Equipment's* series on Great Laboratory Managers in the article [“David Hoyt Booms over Nuclear Magnetic Resonance: Clear Safety Standards and Online Access Protect Instrument Availability.”](#)

EMSL User Featured in *Battelle World*. Kayte Judd, a researcher from the Pacific Northwest National Laboratory, Richland, Washington, who is an EMSL user, was featured in the March 24, 2004, *Battelle World*. She tests ultrasonic sensor capabilities used to control problems for the food processing, chemical, forest products, and consumer products industries. The research is being conducted in PNNL's Food Science and Process Measurement Laboratory.

PNNL-NSF partnership announced. Bill Rogers, EMSL Director, recently announced a formal affiliation between the Pacific Northwest National Laboratory and the National Science Foundation that will enable more university students and faculty to have access to the Environmental Molecular Sciences Laboratory. The Laboratory, EMSL and NSF have negotiated a joint agreement under which NSF will provide supplemental grants of up to \$20,000 to NSF grantees. These supplemental grants support per diem and travel expenses by students, faculty and postdoctoral fellows to conduct research at EMSL using the cadre of outstanding instrumentation and resources. Access a [full description of the program](#).

Visiting Users

Chemistry and Physics of Complex Systems Facility

- Olexandr Bondarchuk, University of Texas, Austin, Texas, worked at EMSL on the study “Atomically Resolved Studies of Transition Metal Oxides.”
- Jinyu Chen, University of California, Berkeley, California, gave the seminar “AFM for the Study of Self-Assembled Films of Oligothiophene: Structure, Conformation and Mechanical Properties.”
- Peter Imrich, State University of New York, Stony Brook, New York, worked at EMSL on the study “Development of Data Analysis and Visualization Software—SpectraMiner.”
- Alexandre Kavetski, Khlopin Radium Institute, St. Petersburg, Russia, worked at EMSL on the study “Electron Stimulated Reactions in Thin Water Films.”

- Ruchuan Liu, Columbia University, New York, New York, gave the seminar “Single Molecule Electron Transfer Dynamics.”
- Luis G. Rodriguez, National Cancer Institute, Bethesda, Maryland, worked on the study “Development of Multi-Functional Microscopy (MFM) for Cancer and AIDS Research.”
- Michael Sheehy, Harvard University, Cambridge, Massachusetts, gave the seminar “Femtosecond-Laser Assisted Incorporation of Dopants in Microstructured Silicon.”
- Yung Doug Suh, Korea Research Institute of Chemical Technology, South Korea, worked at EMSL on the study “Selective Immobilization of Biological Molecules on Single-Walled Carbon Nanotube (SWNT) Surfaces.”

Environmental Spectroscopy and Biogeochemistry Facility

- William P. Ball, Johns Hopkins University, Baltimore, Maryland, and Zheming Wang and Chongxuan Liu, Pacific Northwest National Laboratory, Richland, Washington, collaborated on the characterization of uranyl speciation in aqueous sodium carbonate solutions, sodium carbonate solutions that have been equilibrated with calcite, and sodium carbonate solutions that have been equilibrated with Hanford Site sediments in the pH range from 7 to 10. Both spectroscopic data and results of equilibrium simulations suggest the presence of a series of uranyl species including $(\text{UO}_2)(\text{CO}_3)_3^{4-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$. More work is planned to identify the origin of several additional species.
- Barry Bickmore, Brigham Young University, Provo, Utah, in collaboration with Kevin Rosso, Pacific Northwest National Laboratory, Richland, Washington, extended modeling calculations that attempt to probe acidities of oxyanions in aqueous solution, by performing ab initio molecular dynamics simulations. Dynamics simulations have been performed on phosphoric, carbonic, silicic, and boric acid species in a vacuum and solvated by 32 water molecules to assess the solvent effect on time-averaged bond lengths. The trends found will impact the development of a new multisite complexation model for prediction of M-O(H) bond acidities.
- Cor Hofstee, Netherlands Organization for Applied Scientific Research, Utrecht, Netherlands, in collaboration with Mart Oostrom, Pacific Northwest National Laboratory, Richland, Washington, and EMSL scientist Tom Wietsma, continued experiments investigating both the behavior of a viscous, multicomponent non-aqueous phase liquid (NAPL) in a fluctuating water table system, and its subsequent dissolution. A better understanding of the science issues related to movement of viscous NAPLs and multicomponent dissolution will aid in the remediation of the Hanford Site.
- Jack Istok, Oregon State University, Corvallis, Oregon, in collaboration with Mart Oostrom, Pacific Northwest National Laboratory, Richland, Washington, and EMSL scientist Tom Wietsma, started an experiment designed to elucidate the understanding of the fate and transport of nitrogen gas produced in situ by indigenous nitrate-

reducing organisms. The experiment, which uses porous media from the Natural and Accelerated Bioremediation Research Field Research Center site, is conducted in a newly developed intermediate-scale flow cell, which includes several sampling ports and manometers that allow for the measurement of water pressures. A dual-energy gamma radiation system is used in this experiment to nondestructively and non-intrusively obtain water and nitrogen gas saturation measurements.

- Andy Neal, The University of Georgia Savannah River Ecology Laboratory, Aiken, South Carolina, and Tracy Cail, Oak Ridge National Laboratory, Oak Ridge, Tennessee, in collaboration with Kevin Rosso, Pacific Northwest National Laboratory, Richland, Washington, studied the adhesion of the metal-reducing bacteria *Shewanella* onto various well-defined single crystalline iron-oxide surfaces. A variation of bacterial force spectroscopy was used whereby a single bacterium is attached to an atomic force microscope cantilever and manipulated onto the surface of interest. The forces of bacterium-surface interaction upon surface approach and retraction were measured and compared for the surfaces of hematite (001), magnetite (100), and magnetite (111). Conclusions drawn include identifying a new relationship between the strength of cell adhesion and the ease with which an electron may be transferred from the cell to the surface across the interfacial contact area.
- Jiamin Wan and Joern Larsen, Lawrence Berkeley National Laboratory, Berkeley, California, and Zheming Wang, Pacific Northwest National Laboratory, Richland, Washington, collaborated on the characterization of U(VI) speciation in samples from laboratory batch and column experiments of uranium-contaminated sediments. Comparison of the cryogenic fluorescence spectra of an effluent sample along with three aqueous uranyl species, UO_2^{2+} , $(\text{UO}_2)(\text{CO}_3)_3^{4-}$, and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$, clearly indicated that the fluorescence spectrum of uranyl in the effluent sample closely resembled that of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$. Therefore, it was concluded that uranyl in the effluent is primarily $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$.
- Ken Williams (Figure 20), University of California, Berkeley, Berkeley, California, a Ph.D. student who made his initial visit to the Pacific Northwest National Laboratory at the end of February, returned to EMSL to collaborate with PNNL researcher Alice Dohnalkova and EMSL researcher Jim Young. His area of interest is biomineralization of iron and zinc in flow columns with the bacterium *Desulfovibrio vulgaris*. He uses transmission and scanning electron microscopy for visualization of sites of microbial-mineral interaction. EMSL researcher David McCready provided expertise in X-ray diffraction for analyses of the mineral products.



Figure 20. Ken Williams from the University of California, Berkeley.

High-Field Magnetic Resonance Facility

- Linan An, University of Central Florida, Orlando, Florida, used the 300-MHz CMX NMR spectrometer to run samples for “Solid-State NMR Studies on Structures and Oxidation Behavior of Amorphous SiAlCN Ceramics.”
- Peter Brzovic, University of Washington, Seattle, Washington, used the 600-MHz narrow-bore and 800-MHz NMR spectrometers for the study “NMR Structural Investigations of BRCA1.”
- Kathryn R. Ely and Klara Briknarova, The Burnham Institute, La Jolla, California, sent samples to be run on the 750-MHz NMR spectrometer for the study “Structural Characterization of Free and Fibronectin-bound Anastellin.”
- Scott W. Gordon-Wylie, University of Vermont, Burlington, Vermont, sent samples to be run on the electron paramagnetic resonance spectrometer for the study “EPR and ENDOR Characterization of Fe and Mn Containing Spin Systems of Relevance to Proteins, Magnetic Materials, and Oxidation Catalysts.”
- Nancy W. Hinman, University of Montana, Missoula, Montana, used the 300-MHz CMX NMR spectrometer to run samples for the study “TRAPDOR Experiments on Siliceous Sinters from Thermal Springs.”
- Stephen R. Holbrook, Lawrence Berkeley National Laboratory and the University of California, Berkeley, Berkeley, California, sent samples to be run on the 600-MHz narrow-bore NMR spectrometer for the study “Structural Biology of the Nudix Proteins from the Extremely Radiation-Resistant Bacterium *Deinococcus radiodurans*.”
- Charalampos Kalodimos and Nikolaos Biris, Rutgers University, Newark, New Jersey, sent samples to be run on the 800-MHz NMR spectrometer for “Structural Studies of SecA ATPase, a Critical Component of Protein Translocation Machinery.”
- Gaetano T. Montelione and James Aramini, Rutgers University, Piscataway, New Jersey, sent samples to be run on the 500-MHz narrow-bore, 600-MHz narrow-bore, and 750-MHz NMR spectrometers for the study “Structural Genomics of Eukaryotic Model Organisms.”
- Daniel J. Nielsen, University of Montana, Missoula, Montana, used the 500-MHz NMR spectrometer to run samples for “NMR Studies of Silica-Polyamine Composites.”
- Norma H. Pawley, Los Alamos National Laboratory, Los Alamos, New Mexico, used the 600-MHz narrow-bore and 750-MHz NMR spectrometers for “Structural Studies of the Hyaluronan Receptor CD-44 and CD44-HA Complex.”
- Raymond Reeves, Washington State University, Pullman, Washington, sent samples to be run on the 500-MHz narrow-bore NMR spectrometer for the study “Structural Biology of the Human High Mobility Group A (HMGA) Proteins: Characterizing the Hub of Nuclear Function.”

- Arthur Roberts, University of Washington, Seattle, Washington, used the electron paramagnetic resonance spectrometer to run samples for the study “Drug Interactions of Human and Bacterial Cytochrome P450s Probed by Pulsed Electron Paramagnetic Spectroscopy.”
- Celine Schneider, University of British Columbia, Vancouver, British Columbia, Canada, used the 800-MHz spectrometer to run samples for “Structural Investigations of Solid Materials by High Resolution Solid State NMR at very High Field.”
- Frank D. Soennichsen and Kiattawee Choowongkomon, Case Western Reserve University, Cleveland, Ohio, sent samples to be run on the 800-MHz NMR spectrometer for the study “Structure Determination of Membrane Proteins.”
- Suzana Straus, University of British Columbia, Vancouver, British Columbia, Canada, sent samples to be run on the 800-MHz NMR spectrometer for the study “Development of Resolution Enhancement Techniques for the Complete Structure Determination of Fully $^{13}\text{C}/^{15}\text{N}$ -Labeled Peptides and Proteins Using Solid-State NMR.”
- Thomas C. Terwilliger, Los Alamos National Laboratory, Los Alamos, New Mexico, sent samples to be run on the 500-MHz narrow-bore NMR spectrometer for the study “Structural Proteomics of *Myobacterium tuberculosis*.”
- Gabriele Varani, Thomas C. Leeper, and Steve L. Reichow, University of Washington, Seattle, Washington, sent samples to be run on the 600-MHz narrow-bore NMR spectrometer for the study “Structure of Telomerase RNA and Telomeric Proteins.”
- Susan S. Wallace, University of Vermont, Burlington, Vermont, sent samples to be run on the 500-MHz narrow-bore and 600-MHz NMR spectrometers for the study “Interaction of *Escherichia coli* Formamidopyrimidine-DNA Glycosylase (Fpg) with Damaged DNA Containing an 7,8-Dihydro-8-oxoguanine Lesion.”

High Performance Mass Spectrometry Facility

- Matthew A. Coleman, Lawrence Livermore National Laboratory, Livermore, California, sent samples to be run on the LCQ spectrometers for the study “Identification of Proteins Differentially Expressed in Response IR.”
- Steven Gross and Sylvia Cermelli, University of California, Irvine, Irvine, California, sent immunoprecipitates of a particular protein of interest (Lipid Storage Droplet 2), found in *Drosophila*, for further processing and subsequent analysis by LC-MS/MS. Lipid droplets are involved in cellular transport and are being studied to better understand cellular transport mechanisms. Sample processing at EMSL included a tryptic digestion technique specific to hydrophobic proteins, followed by a sample "washing" procedure required for successful LC-MS/MS analysis. Analysis was performed on an EMSL-constructed high-performance liquid chromatography system using reverse-phase chromatography, electrospray ionization, and a Finnigan ion-trap mass spectrometer.

- Michael Katze, Deborah Diamond, and Eric Chan, University of Washington, Seattle, Washington, are incorporating into a manuscript for publication the data generated from analysis of HCV-infected cell culture samples and liver biopsy samples. This manuscript will provide information that demonstrates application of the team's methodologies toward the analysis of HCV infection and reports preliminary results on the observed biological effects of virus infection.
- Sandra McCutchen-Maloney, Lawrence Livermore National Laboratory, Livermore, California, and Mary Lipton, Pacific Northwest National Laboratory, Richland, Washington, are currently finishing qualitative and quantitative analysis of the whole proteome of *Yersinia pestis*.
- Wendy Shaw, Patrick Stayton, and Allison Golden, University of Washington, Seattle, Washington, provided samples for analysis of phosphopeptides. An extensive effort is also under way to find two specific proteins in low abundance within the samples.

Interfacial and Nanoscale Science Facility

- Jiji Antony, University of Idaho, Moscow, Idaho, used the surface science and electron microscopy suites to investigate properties of iron nanoparticles.
- Zsuzsanna Balogh, Washington State University, Pullman, Washington, used the electron microscopy suite to perform a scanning electron microscopy investigation of soil mineral weathering.
- Amit Bandyopadhyay, Washington State University, Pullman, used the electron microscopy suite to characterize zirconium-based bulk amorphous alloys.
- Susmita Bose, Washington State University, Pullman, Washington, used the electron microscopy suite to characterize nanostructured ceramics.
- Robin Catalano, University of Virginia, Charlottesville, Virginia, used the oxide molecular beam epitaxy facility to investigate the growth of niobia nanostructures on TiO₂ substrates.
- Rafail Khairoutdinov, University of Alaska, Fairbanks, Alaska, used the sputter deposition capability to investigate the growth of metal layers on carbon nanotubes.
- Julia Martinez, Washington State University, Pullman, used the X-ray diffraction facility to characterize lead-zirconate-titanate (PZT) films.
- Vince Rundhaug, Columbia Gem and Jewelry, Kennewick, Washington, visited the X-ray diffraction facility to explore future collaborations.
- Richard Smith, Asghar Kayani, and Chipitalapatte Raman, Montana State University, Bozeman, Montana, used the accelerator facility to investigate the properties of multilayer-coated corrosion-resistant films for solid-oxide fuel cell applications.

- Kenneth Williams, Lawrence Berkeley National Laboratory, Berkeley, California, used the electron microscopy suite for imaging and characterization of pore-scale phenomena such as microbial attachment, iron- and zinc-sulfide precipitates and microbe-metal associations in their Environmental Management Science Program.

Molecular Science Computing Facility

- Tahir Cader, Ryan Baddeley, and Kirby Krause, Isothermal Systems Research, Spokane, Washington, reviewed the data for the SprayCool Project with members of the Molecular Science Computing Facility Operations group. Also involved during this review were Allan Knies, Michael Peterson, David Barkai, Chris Schaenig, John Calhoun, and James Malone of Intel Americas, Inc., Santa Clara, California.
- Antonio Ferreira, University of Memphis, Memphis, Tennessee, visited EMSL to discuss adding semi-empirical methods into NWChem. He began addressing architecture issues with the Molecular Science Software Group and will continue this work from the University of Memphis.
- Karol Kowalski, Michigan State University, East Lansing, Michigan, gave a seminar entitled "Method of Moments of Coupled-Cluster Equations: A New Tool in Many-Body Quantum Theory." He is a leader in the field of accurate many-body theories and is internationally respected for his creative research on novel coupled-cluster theories and algorithms (not only for atoms and molecules, but also for nuclei).
- Chikaodinaka Nwankpa, Drexel University, Philadelphia, Pennsylvania; Sotirios Ziavras, New Jersey Institute of Technology, Newark, New Jersey; Phil Overholt, DOE, Washington, D.C.; and Stephen Waslo, DOE, Argonne, Illinois met with PNNL staff, including Scott Studham, Technical Lead of the Molecular Science Computing Facility's Operations Group, to discuss a research and development exercise to simulate real-time, reconfigurable electric power grids. The tools being developed will allow analysis of various types of actual power system events and their consequences, including line contingencies and generator outages on a large-scale electric power network. The simulations will enable real-time risk weighted response options and will also be used for advanced training methods on power system operation.

Molecular Sciences Software - New User Agreements with NWChem/Ecce

- Adam Mickiewicz University, Poznan, Poland
- AGH University of Science and Technology, Krakow, Poland
- Aurigene Discovery Technologies, Bangalore, India
- Brigham Young University, Provo, Utah
- Carnegie Mellon University, Pittsburgh, Pennsylvania
- Catholic University of Korea, Puchon City, Korea
- Chulalongkorn University, Bangkok, Thailand
- Comenius University, Bratislava, Slovakia
- De Novo Pharmaceuticals, Cambridge, United Kingdom

- Degussa, Hanau, Germany
- Estonian Educational and Research Network, Tartu, Estonia
- Gdansk University of Technology, Gdansk, Poland
- Hamilton College, Clinton, New York
- Harvard University, Cambridge, Massachusetts
- Hefei University of Technology, Hefei, China
- IBM, Mendota Heights, Minnesota
- Institute of Biochemical Physics RAS, Moscow, Russia
- Institute of Surface Chemistry of National Academy of Science of Ukraine, Kiev, Ukraine
- ISPN, Innovation for Patient Care, Les ULIS Cedex, France
- Leiden University, Leiden, Netherlands
- Lund University, Lund, Sweden
- Moscow State University, Moscow, Russia
- National Research Council of Canada, Ottawa, Ontario, Canada
- NEC High Performance Computing Europe GmbH, Grosskarolinenfeld, Germany
- North Dakota State University, Fargo, North Dakota
- Northwestern University, Evanston, Illinois
- Octigabay, Burnaby, British Columbia, Canada
- Penguin Computing, San Francisco, California
- Pennsylvania State University, University Park, Pennsylvania
- Proteologics, Rehovot, Israel
- QMolecular Ltd, Darlington, Great Britain
- Russian Academy of Science, Moscow, Russia
- Sarnoff Corporation, Princeton, New Jersey
- The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong
- The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong
- The University of Electro-Communications, Tokyo, Japan
- Universidade Estadual de Campinas, Campinas, Brazil
- Università degli Studi del Piemonte Orientale Amedeo Avogadro, Alessandria, Italy
- University de Madam Curie, Paris, France
- University of Asia and the Pacific, Pasig City, Metro Manila, Philippines
- University of Bristol, Bristol, United Kingdom
- University of California, Merced, Merced, California
- University of Cologne, Cologne, Germany
- University of Ferrara, Ferrara, Italy
- University of Illinois, Urbana, Illinois
- University of Manitoba, Winnipeg, Manitoba, Canada
- University of Minnesota, Minneapolis, Minnesota
- University of South Florida, Tampa, Florida
- University of Tennessee, Memphis, Tennessee
- Whitman College, Walla Walla, Washington
- Wroclaw Centre for Networking and Supercomputing, Wroclaw, Poland
- Wroclaw University of Technology, Wroclaw, Poland

New Staff

Following an extended leave, Tina Foley returned to EMSL as a Senior Administrative Assistant in the Molecular Science Computing Facility Visualization and User Services group. Previously a Program Administrator in the User Services Office, Tina worked with pre-EMSL groups since 1989, benchmarking other labs for best practices, designing EMSL Ops (later called IOPS, an integrated operations system for developing the Environment, Safety and Health program of a building or facility), monitoring user satisfaction, and contributing to the redesign of the EMSL User (proposal) System.

Publications

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

Autrey T, AK Brown, DM Camaioni, M Dupuis, NS Foster, and A Getty. 2004. "Thermochemistry of Aqueous Hydroxyl Radical from Advances in Photoacoustic Calorimetry and ab Initio Continuum Solvation Theory." *Journal of the American Chemical Society* 126(12):3680-3681.

Banisaukas J, J Szczepanski, M Vala, and S Hirata. 2004. "Vibrational and Electronic Absorption Spectroscopy of 2,3-Benzofluorene and its Cation. Photodissociation Pathways of the Cation." *Journal of Physical Chemistry A* 108(17):3713-3722.

Bargar JR, TP Trainor, JP Fitts, SA Chambers, and GE Brown, Jr. 2004. "In Situ Grazing-Incidence Extended X-ray Absorption Fine Structure Study of Pb(II) Chemisorption on Hematite (0001) and (1 $\bar{1}$ 02) Surfaces." *Langmuir* 20(5):1667-1673.

Belov ME, GA Anderson, MA Wingerd, HR Udseth, K Tang, DC Prior, KR Swanson, MA Buschbach, EF Strittmatter, RJ Moore, and RD Smith. 2004. "An Automated High Performance Capillary Liquid Chromatography-Fourier Transform Ion Cyclotron Resonance Mass Spectrometer for High-Throughput Proteomics." *Journal of the American Society for Mass Spectrometry* 15(2):212-232.

Cooley JW, AG Roberts, MK Bowman, DM Kramer, and F Daldal. 2004. "The Raised Midpoint Potential of the [2Fe2S] Cluster of Cytochrome bc1 is Mediated by Both the Qo Site Occupants and the Head Domain Position of the Fe-S Protein Subunit." *Biochemistry* 43(8):2217-2227.

Elliott DC, GG Neuenschwander, TR Hart, RS Butner, AH Zacher, MH Engelhard, JS Young, and DE McCready. 2004. "Chemical Processing in High-Pressure Aqueous Environments. 7. Process Development for Catalytic Gasification of Wet Biomass Feedstocks." *Industrial & Engineering Chemistry Research* 43(9):1999-2004.

Foster NS, NB Valentine, SE Thompson, TJ Johnson, and JE Amonette. 2004. "FTIR Transmission and Photoacoustic Spectroscopy for the Statistical Identification of Bacteria." *In Proceedings of SPIE - Chemical and Biological Point Sensors for Homeland Defense Symposium*, vol. 5269, ed. Arthur J. Sedlacek III, Steven D. Christensen, Richard Colto, pp. 172-182. SPIE (International Society for Optical Engineering), Bellingham, Washington.

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.

- Gao F, M Posselt, V Belko, Y Zhang, and WJ Weber. 2004. "Structures and Energetics of Defects: A Comparative Study of 3C- and 4H-SiC." *Nuclear Instruments and Methods in Physics Research. Section B, Beam Interactions with Materials and Atoms* 218:74-79.
- Gross GM, JW Grate, and RE Synovec. 2004. "Monolayer-Protected Gold Nanoparticles as an Efficient Stationary Phase for Open Tubular Gas Chromatography Using a Square Capillary: Model for Chip-Based Gas Chromatography in Square Cornered Microfabricated Channels." *Journal of Chromatography A* 1029(1-2):185-192.
- Gu W, SJ Rahi, and V Helms. 2004. "Solvation Free Energies and Transfer Free Energies for Amino Acids from Hydrophobic Solution to Water Solution from a Very Simple Residue Model." *Journal of Physical Chemistry B* 108(18):5806-5814.
- Hager JS, J Zahardis, RM Pagni, RN Compton, and J Li. 2004. "Raman Under Nitrogen. The High-Resolution Raman Spectroscopy of Crystalline Uranocene, Thorocene, and Ferrocene." *Journal of Chemical Physics* 120(6):2708-2718.
- Harms G, G Orr, and HP Lu. 2004. "Probing Ion Channel Conformational Dynamics Using Simultaneous Single-Molecule Ultrafast Spectroscopy and Patch-Clamp Electric Recording." *Applied Physics Letters* 84(10):1792-1794.
- 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.
- Hoyt DW, SD Burton, MR Peterson, JD Myers, and G Chin, Jr. 2004. "Expanding Your Laboratory by Accessing Collaboratory Resources." *Analytical and Bioanalytical Chemistry* 378(6):1408-1410.
- Jiang W, CM Wang, WJ Weber, MH Engelhard, and LV Saraf. 2004. "Direct Determination of Volume Changes in Ion-Beam-Irradiated SiC." *Journal of Applied Physics* 95(9):4687-4690.
- Jiang W, WJ Weber, LM Wang, and K Sun. 2004. "Amorphization Processes in Au Ion Irradiated GaN at 150 - 300 K." *Nuclear Instruments and Methods in Physics Research. Section B, Beam Interactions with Materials and Atoms* 218:427-432.
- Johnson TJ, BA Roberts, and JF Kelly. 2004. "Semiactive Infrared Remote Sensing: A Practical Prototype and Field Comparison." *Applied Optics: Optical Technology and Biomedical Optics* 43(3):638-650.
- Kim S, Z Zhang, S Upchurch, NG Isern, and Y Chen. 2004. "Structure and DNA-Binding Sites of the SWI1 AT-Rich Interaction Domain (ARID) Suggest Determinants for Sequence-Specific DNA Recognition." *Journal of Biological Chemistry* 279(16):16670-16676.
- Kuster WC, BT Jobson, T Karl, D Riemer, E Apel, PD Goldan, and FC Fehsenfeld. 2004. "Intercomparison of Volatile Organic Carbon Measurement Techniques and Data at La

Porte during the TexAQS2000 Air Quality Study." *Environmental Science & Technology* 38(1):221-228.

Laskin J. 2004. "Energetics and Dynamics of Peptide Fragmentation from Multiple-Collision Activation and Surface-Induced Dissociation Studies." *European Journal of Mass Spectrometry* 10(2):259-267.

Li J, BE Bursten, LS Andrews, and CJ Marsden. 2004. "On the Electronic Structure of Molecular UO₂ in the Presence of Ar Atoms: Evidence for Direct U-Ar Bonding." *Journal of the American Chemical Society* 126(11):3424-3425.

Lipton AS, RW Heck, JA Sears, and PD Ellis. 2004. "Low Temperature Solid-State NMR Experiments of Half-Integer Quadrupolar Nuclides: Caveats and Data Analysis." *Journal of Magnetic Resonance* 168(1):66-74.

Liu SR, Z Dohnalek, RS Smith, and BD Kay. 2004. "Interaction of CH₄, CH₃Cl, CH₂Cl₂, CHCl₃, and CCl₄ with O-terminated FeO(111)." *Journal of Physical Chemistry B* 108(11):3644-3650.

Micic M, N Klymyshyn, and HP Lu. 2004. "Finite Element Method Simulations of the Near-Field Enhancement at the Vicinity of Fractal Rough Metallic Surfaces." *Journal of Physical Chemistry B* 108(9):2939-2947.

Ostrom M, TW Wietsma, and NS Foster. 2004. "The Subsurface Flow and Transport Experimental Laboratory: A New Department of Energy User's Facility for Intermediate-Scale Experimentation." In *American Geophysical Union Hydrology Days*, ed. J. Ramirez, pp. 182-189. American Geophysical Union (AGU), Washington DC.

Palumbo AV, JF McCarthy, JE Amonette, LS Fisher, SD Wullschleger, and WL Daniels. 2004. "Prospects for Enhancing Carbon Sequestration and Reclamation of Degraded Lands with Fossil-Fuel Combustion By-Products." *Advances in Environmental Research* 8(3-4):425-438.

Rosso KM and M Dupuis. 2004. "Reorganization Energy Associated with Small Polaron Mobility in Iron Oxide." *Journal of Chemical Physics* 120(15):7050-7054.

Rosso KM, DM Smith, Z Wang, CC Ainsworth, and JK Fredrickson. 2004. "Self-Exchange Electron Transfer Kinetics and Reduction Potentials for Anthraquinone Disulfonate." *Journal of Physical Chemistry A* 108(16):3292-3303.

Rustad JR, KM Rosso, and AR Felmy. 2004. "Molecular Dynamics Investigation of Ferrous-Ferric Electron Transfer in a Hydrolyzing Aqueous Solution: Calculation of the pH Dependence of the Diabatic Transfer Barrier and the Potential of Mean Force." *Journal of Chemical Physics* 120(16):7607-7615.

Studham RS. 2004. "The Commoditization of High Performance Storage: Breaking Into the Next Frontier." *Scientific Computing & Instrumentation* 21(5):14, 48.

Szanyi J, J Kwak, and CH Peden. 2004. "The Effect of Water on the Adsorption of NO₂ in Na- and Ba-Y, FAU Zeolites: A Combined FTIR and TPD Investigation." *Journal of Physical Chemistry B* 108(12):3746-3753.

Tanimura K and WP Hess. 2004. "Temperature-Dependent Yield of Frenkel Pairs Generated by Valence Excitation in NaCl." *Physical Review B* 69:155102.

Thevuthasan S, V Shutthanandan, CM Wang, WJ Weber, W Jiang, A Cavanagh, J Lian, and LM Wang. 2004. "Ion-Beam Synthesis of Epitaxial Au Nanocrystals in MgO." *Journal of Materials Research* 19(5):1311-1314.

Wang CM, V Shutthanandan, Y Zhang, LE Thomas, DR Baer, S Thevuthasan, and G Duscher. 2004. "Precipitation of Au Nanoclusters in SrTiO₃ by Ion Implantation." *Journal of Applied Physics* 95(9):5060-5068.

Weber WJ, F Gao, R Devanathan, and W Jiang. 2004. "The Efficiency of Damage Production in Silicon Carbide." *Nuclear Instruments and Methods in Physics Research. Section B, Beam Interactions with Materials and Atoms* 218:68-73.

White JM, J Szanyi, and MA Henderson. 2004. "Thermal Chemistry of Trimethyl Acetic Acid on TiO₂(110)." *Journal of Physical Chemistry B* 108(11):3592-3602.

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Zachara JM, RK Kukkadapu, PL Gassman, A Dohnalkova, JK Fredrickson, and T Anderson. 2004. "Biogeochemical Transformation of Fe Minerals in a Petroleum-Contaminated Aquifer." *Geochimica et Cosmochimica Acta* 68(8):1791-1805.

Zhai HJ, AN Alexandrova, KA Birch, AI Boldyrev, and LS Wang. 2003. "Hepta- and Octacoordinate Boron in Molecular Wheels of Eight- and Nine-Atom Boron Clusters: Observation and Confirmation." *Angewandte Chemie International Edition* 42(48):6004-6008.

Zhang Y, V Shutthanandan, R Devanathan, S Thevuthasan, DE McCready, JS Young, G Balakrishnan, DM Paul, and WJ Weber. 2004. "Damage Accumulation and Amorphization in Samarium Titanate Pyrochlore." *Nuclear Instruments and Methods in Physics Research. Section B, Beam Interactions with Materials and Atoms* 218:89-94.

Zhang Y, WJ Weber, V Shutthanandan, R Devanathan, S Thevuthasan, G Balakrishnan, and DM Paul. 2004. "Damage Evolution on Sm and O Sublattices in Au-Implanted Samarium Titanate Pyrochlore." *Journal of Applied Physics* 95(5):2866-2872.

Zhang Y, WJ Weber, W Jiang, CM Wang, V Shutthanandan, and A Hallen. 2004. "Effects of Implantation Temperature on Damage Accumulation in Al-Implanted 4H-SiC." *Journal of Applied Physics* 95(8):4012-4018.

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.

Amonette JE, J Kim, and CK Russell. 2004. "Enhancement of Soil Carbon Sequestration: A Catalytic Approach." Presented by James E. Amonette (Invited Speaker) at the 227th American Chemical Society National Meeting, Anaheim, California, on March 30, 2004.

Anderson GA. 2004. "Managing Large Data Sets." Presented by Gordon Anderson (Invited Speaker) at the American Association for the Advancement of Science Meeting, Seattle, Washington, on February 15, 2004.

Anderson GA, MS Lipton, GR Kiebel, DA Clark, KJ Auberry, EA Livesay, V Kery, BS Hooker, ES Peterson, L Pasa-Tolic, ME Monroe, MF Romine, JK Fredrickson, YA Gorby, N Tolic, GS Michaels, and RD Smith. 2004. "Pilot Proteomics Production Pipeline." Presented by Gordon Anderson (Invited Speaker) at the Genomes to Life Program Workshop, Washington, D.C., on March 1, 2004.

Ayotte P, JL Daschbach, Z Dohnalek, GA Kimmel, RS Smith, KP Stevenson, and GR Teeter. 2004. "Molecular Beam Studies of Nanoscale Films of Amorphous Solid Water." Presented by Bruce D. Kay (Invited Speaker) at the American Physical Society March Meeting, Montreal, Quebec, Canada, on March 23, 2004.

Baer DR, JE Amonette, J Antony, JC Linehan, DW Matson, KH Pecher, RL Penn, Y Qiang, and PG Tratnyek. 2004. "Characterization and Properties of Iron and Iron-Oxide Nanoparticles." Presented by Don R. Baer (Invited Speaker) at the 227th American Chemical Society National Meeting, Anaheim, California, on March 28, 2004.

Beck KM, M Henryk, AG Joly, and WP Hess. 2004. "Morphological Changes in Irradiated MgO Nanofibers Detected Via SEM and Neutral Atom Desorption Spectroscopy." Presented by Ken Beck (Invited Speaker) at the COST working group entitled: Chemical Reactivity of Metal Oxide Nanostructure, Turnin, on April 4, 2004.

Biju VP, M Micic, D Hu, and HP Lu. 2004. "Intermittent Single-Molecule Interfacial Electron Transfer Dynamics in Dye-TiO₂ Nanoparticle Systems." Presented by Vasudevanpillai Biju at the Annual American Physical Society March 2004 Meeting, Montreal, Quebec, Canada, on March 24, 2004.

Bylaska EJ, KL Tsemekhman, and H Jonsson. 2004. "Self-Consistent Self-Interaction Corrected DFT: The Method and Applications to Extended and Confined Systems." Presented by Eric J. Bylaska at the American Physical Society 2004 March Meeting, Montreal, Quebec, Canada, on March 23, 2004.

Cort JR, R Xiao, Y Chiang, G Montelione, and MA Kennedy. 2004. "NMR Structure of 5,10-Methenyltetrahydrofolate Synthetase from *Aquifex aeolicus*." Presented by John Cort at the 2004 Keystone Symposium - Structural Genomics, Salt Lake City, Utah, on April 10, 2004.

Cowin JP and MJ Iedema. 2004. "Structured Liquids: Custom-Built to Explore Transport at Liquid Interfaces." Presented by James Cowin at the American Physical Society March Meeting, Montreal, Quebec, Canada, on March 23, 2004.

Farnan I, HM Cho, WJ Weber, RD Scheele, NR Johnson, and AE Kozelisky. 2004. "Magic-Angle Spinning NMR of Highly Radioactive Ceramics: ^{29}Si NMR Zircons Containing 10wt% ^{239}Pu and ^{238}Pu ." Presented by Ian Farnan at the Experimental NMR Conference, Asilomar, California, on April 18, 2004.

Gannon PE, CR Tripp, A Knospe, CV Ramana, M Deibert, RJ Smith, VI Gorokhovskiy, V Shutthanandan, and DS Gelles. 2004. "High Temperature Oxidation Resistance and Surface Electrical Conductivity of Stainless Steel with Filtered Arc CrAlN Superlattice Multilayer Coatings." Presented by Dick Smith at the International Conference on Metal Coatings and Thin Films, San Diego, California, on April 15, 2004.

Grate JW and J Kim. 2004. "Single Enzyme Nanoparticles: A New Nanostructure for Enzyme Stabilization." Presented by Jay W. Grate and Jungbae Kim at the 2004 Materials Research Society Spring Meeting, San Francisco, California, on April 13, 2004.

Hess WP, AG Joly, KM Beck, JT Dickinson, PV Sushko, and A Shluger. 2004. "Time-Resolved fs and Tunable ns Laser Desorption from Ionic Crystals." Presented by Wayne Hess (Invited Speaker) at the SPIE International Symposium, Taos, New Mexico, on April 25, 2004.

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

Hirata S. 2004. "Science with R. J. Bartlett: Extended Systems; Ab Initio DFT; Coupled-Cluster Theory." Presented by So Hirata (Invited Speaker) at the Systematic Treatment of Electron Correlation, Brunswick, Georgia, on April 24, 2004.

Isern NG, JA Sears, JJ Ford, SD Burton, DN Rommereim, PD Ellis, and DW Hoyt. 2004. "High Field Magnetic Resonance Facility: Capabilities and Access to Our National User Facility." Presented by Nancy Isern at the 45th ENC Experimental Nuclear Magnetic Resonance Conference 2004, Pacific Grove, California, on April 18, 2004.

Kennedy MA, K McAteer, GW Buchko, A Aceves-Gaono, R Michalczyk, LA Silks, and JH Miller. 2004. "Use of Multiple Specifically-Labeled DNA Oligomers to Study Global DNA Curvature and the Structure of HMGA1-DNA Complex." Presented by Michael Kennedy at the 45th ENC Experimental Nuclear Magnetic Resonance Conference, Pacific Grove, California, on April 20, 2004.

Kim N, MK Bowman, and VJ DeRose. 2004. "Monitoring Tertiary Interactions in the Hammerhead Ribozyme Using Pulsed EPR Spectroscopy." Presented by Nak-Kyoon Kim at the Biophysical Society Meeting, Baltimore, Maryland, on February 14, 2004.

Krueger BJ, VH Grassian, JP Cowin, and A Laskin. 2004. "Hydration Reactivity of Individual Calcium Containing Mineral Dust Particles Aged with Nitric Acid." Presented by Alex Laskin (Invited Speaker) at the American Physical Society March Meeting, Montreal, Quebec, Canada, on March 24, 2004.

Laskin J. 2004. "Entropy Effects in the Gas Phase Dissociation of Peptides and Proteins." Presented by Julia Laskin (Invited Speaker) at the Euresco Conference, Exeter, United Kingdom, on April 13, 2004.

Liu C, JM Zachara, JP McKinley, Z Wang, and PD Majors. 2004. "Influence of Microscopic Diffusive Process on Uranyl Precipitation and Dissolution in Subsurface Sediments at Hanford Site, U.S.A." Presented by Chongxuan Liu at the 227th American Chemical Society National Meeting, Anaheim, California, on March 30, 2004.

Lu HP. 2004. "Single-Molecule Protein Recognition and Reaction Dynamics." Presented by Peter Lu (Invited Speaker) at SMBU 2004, Takamatsu City, Japan, on March 22, 2004.

McAteer K, GW Buchko, R Michalczyk, A Aceves-Gaona, S Ni, JH Miller, RC Reeves, and MA Kennedy. 2004. "Use of Multiple, Specifically-Labeled DNA Oligomers to Study Global DNA Curvature and the Structure of the Mammalian Non-Histone Chromatin Protein (HMGA1) Associated With A•T-Rich DNA." Presented by Garry Buchko at the VIIIth International Workshop on Radiation Damage to DNA, Banff, Alberta, Canada, on May 24, 2004.

Nachimuthu P, S Thevuthasan, WJ Weber, V Shutthanandan, Y Zhang, DK Shuh, DW Lindle, G Balakrishnan, DM Paul, EM Gullikson, and RC Perera. 2004. "Structural and Electronic Properties of $A_2Ti_2O_7$ (A=Sm, Gd, Ho, and Yb) Pyrochlores following Ion-beam Irradiation: A Ti 2p and O 1s NEXAFS Study." Presented by P. Nachimuthu at the 2004 Spring MRS Meeting, San Francisco, California, on April 14, 2004.

Petrik NG and GA Kimmel. 2004. "Electron-Stimulated Production of Molecular Hydrogen in Thin Water Films Adsorbed on Pt(111)." Presented by N. G. Petrik (Invited Speaker) at the American Physical Society March Meeting, Montreal, Quebec, Canada, on March 20, 2004.

Rosso KM and M Dupuis. 2004. "Charge Transport in Metal Oxides." Presented by Michel Dupuis (Invited Speaker) at Theory and Applications of Computational Chemistry, Gyeongju, Korea, on February 15, 2004.

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