

EMSL Report
September/October 2003

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Research Highlights

Charge Transport in Micas: The Kinetics of $\text{Fe}^{\text{II/III}}$ Electron Transfer in the Octahedral Sheet

KM Rosso^(a) and ES Ilton^(a)

(a) Pacific Northwest National Laboratory, Richland, Washington

The two principal $\text{Fe}^{\text{II/III}}$ electron exchange reactions underlying charge transport in the octahedral sheet of ideal end-member annite (Figure 1) were modeled using a combination of *ab initio* calculations and Marcus electron transfer theory. A small polaron model was applied, which yielded electron-hopping activation energies that agree well with the limited available experimental data. A small *ab initio* cluster model successfully reproduced several important structural, energetic, and magnetic characteristics of the M1 and M2 iron sites in the annite octahedral sheet. The cluster enabled calculation of the internal reorganization energy and electronic coupling matrix elements for the M2–M2 and M1–M2 electron transfer reactions. The M2–M2 electron transfer is symmetric with a predicted forward/reverse electron-hopping rate of 106 s^{-1} . The M1–M2 electron transfers are asymmetric due to the higher ionization potential by 0.46 eV of Fe^{II} in the M1 site. The electronic coupling matrix elements for these reactions are predicted to be small and of similar magnitude, suggesting the possibility that the coupling is essentially direction-independent amongst hopping directions in the octahedral sheet. M1 iron sites are predicted to be efficient electron traps, and charge transport should occur by nearest-neighbor electron hops along the M2 iron sublattice.

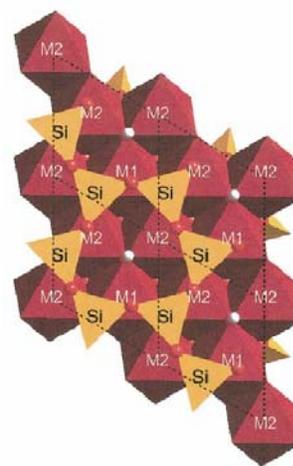


Figure 1. The polyhedral structure of the 2:1 layer of idealized annite as viewed down [001]. Al/Si substitution has been removed for clarity, which also corresponds to the charge neutral 2:1 layer case. Two unique Fe^{II} sites comprise the octahedral sheet, M1 and M2.

Protein Structures from the Northeast Structural Genomics Consortium Determined Using NMR Data Collected at EMSL

JR Cort,^(a) B Wu,^(b) JM Aramini,^(c) TA Ramelot,^(a) CH Arrowsmith,^(b) GT Montelione,^(c) and MA Kennedy^(a)

(a) Pacific Northwest National Laboratory, Richland, Washington

(b) University of Toronto, Toronto, Ontario, Canada

(c) Rutgers University, Piscataway, New Jersey

Past genome sequencing projects have demonstrated that all organisms contain thousands of proteins whose structures cannot be predicted on the basis of amino acid sequence similarity to other proteins of known structure. A large fraction of these proteins is functionally uncharacterized as well. Determination of the three-dimensional, high-resolution structure of these proteins aids the discovery of their molecular and cellular functions. Collectively, the growing database of protein structures will help scientists better understand the breadth and depth of form and function within the protein repertoire. This endeavor is termed structural genomics.

The Northeast Structural Genomics Consortium (NESG) (www.nesg.org) is a pilot project funded under the Protein Structure Initiative of the National Institutes of Health, and is headed by G.T. Montelione, Rutgers University, Piscataway, New Jersey. The NESG uses both solution nuclear magnetic resonance (NMR) spectroscopy and X-ray crystallography for high-throughput structure determination of structurally or functionally uncharacterized proteins from a wide range of organisms. The NESG is a major user of EMSL's high-field (600 MHz or greater) NMR instruments. For each protein, a sample labeled with ^{13}C and ^{15}N is used for the multidimensional triple resonance experiments conducted to determine spectral assignment and structure. Typically, a set of experiments requiring four to six weeks of instrument time is collected for a single protein sample. Subsequently, several weeks or more are required to analyze the data and extract the information required to calculate and refine the structure. For other samples, only a subset of experiments (usually NOESYs) which best utilizes the high field spectrometers is collected at EMSL, and the rest are collected at other NESG institutions. A principal goal of the NESG project is the development of a high-throughput structure determination process, and much of the project's effort is aimed at increasing the efficiency with which the necessary data can be acquired.

Figures 2 through 5 are some of the structures determined during the last year from data sets collected entirely at EMSL. All have been deposited in the Protein Data Bank.

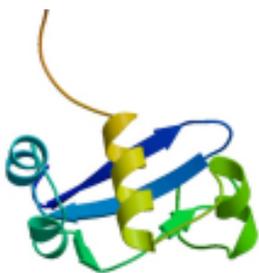


Figure 2. Structure of *S. cerevisiae* YHR087W (NESG ID YTYst425, PDB ID 1NYN). This protein had no sequence homologs except in other fungi, but it bore strong structural resemblance to a domain of human disease protein. Structure comparison of the two proteins reveals common features that are likely to be functionally important. Further characterization based on this resemblance is ongoing.

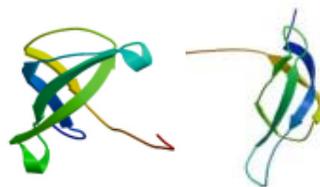


Figure 3. Structures of *P. horikoshii* and *M. thermoautotrophicus* ribosomal protein S28E (NESG IDs JR19 & TT744, PDB IDs 1NY4 & 1NE3). These two archaeal proteins are components of the ribosome in their host organisms. Structural studies of individual ribosomal proteins help researchers understand protein-RNA interactions during assembly of the ribosome and in the intact, functional ribosome.



Figure 4. Structure of *H. influenzae* IscU (NESG ID IR24, PDB ID 1Q48). IscU is known to be involved in iron-sulfur cluster assembly; however, the molecular mechanism of this involvement is a mystery. Functional characterization aimed at understanding this mechanism is currently under way.

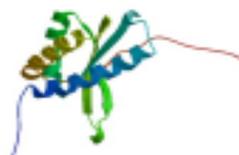


Figure 5. Structure of *V. cholerae* VC0424 (NESG ID OP3, PDB ID 1NXI). VC0424 is a conserved bacterial protein of unknown function. Analysis of the structure revealed a cleft containing many conserved residues; such features may indicate a binding site, but no ligand has been found yet.

Measurement of the Band Offsets between Amorphous LaAlO₃ and Silicon

LF Edge,^(a) DG Schlom,^(a) SA Chambers,^(b) E Cicerrella,^(c) JL Freeouf,^(c) B Holländer,^(d) and J Schubert^(d)

(a) Pennsylvania State University, University Park, Pennsylvania

(b) Pacific Northwest National Laboratory, Richland, Washington

(c) Oregon Health and Sciences University, Portland, Oregon

(d) Institut für Schichten und Grenzflächen ISG1-IT, Jülich, Germany

Currently, extensive research is being conducted to find alternative gate dielectrics to replace silicon dioxide (SiO₂) in metal oxide semiconductor field-effect transistors (MOSFETs) as SiO₂ approaches its fundamental limits. LaAlO₃ is a promising alternative gate dielectric. Single-crystalline LaAlO₃ has a dielectric constant of 24.1 ± 0.2 measured at 145 GHz and an optical bandgap of 5.6 eV. Amorphous LaAlO₃ thin films on silicon have an estimated dielectric constant of 20 to 25. It has also been shown that single-crystalline LaAlO₃ is stable in contact with silicon under standard MOSFET processing conditions of 1026°C for 20 seconds. The band offsets between LaAlO₃ and silicon have been predicted to be in the range 1.0 to 2.1 eV for electrons and 1.9 to 3.5 eV for holes. All of these properties meet the requirements for an alternative gate dielectric as suggested by the 2001 edition of the *International Technology Roadmap for Semiconductors*.

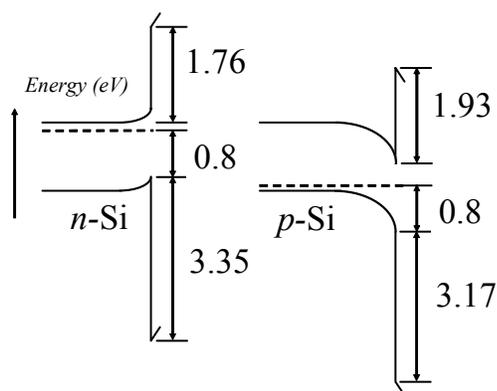


Figure 6. Type I means that the band gap of silicon is entirely encased within the band gap of LaAlO₃.

Although LaAlO₃/silicon shows many promising properties, there are no published papers that have experimentally determined band offsets. It is critical that the high K gate dielectric has conduction and valence band offsets ≥ 1 eV for both electrons and holes from the silicon. To this end, the band offsets between amorphous LaAlO₃ and silicon have been determined from X-ray photoelectron spectroscopy. These films, which are free of interfacial SiO₂, were made using molecular beam deposition at Pennsylvania State University. The band offsets were measured at EMSL by Pennsylvania State University and PNNL researchers. The band lineup is type I with measured band offsets of 1.86 ± 0.2 eV for electrons and 3.23 ± 0.1 eV for holes. Type I means that the band gap of silicon is entirely encased within the band gap of LaAlO₃, as shown in Figure 6. The band offsets are independent of the doping concentration in the silicon substrate as well as the LaAlO₃ film thickness, as seen in Table 1. These amorphous LaAlO₃ films have a bandgap of 6.2 ± 0.1 eV, as measured by researchers from Oregon Health and Sciences University. The fact that

the offsets at both band edges exceed 1 eV means that LaAlO₃ is a very attractive candidate for a next-generation gate oxide in silicon MOSFETs with low leakage current.

Table 1. Band offsets in silicon substrate and LaAlO₃ film.

Film	ΔE_c (eV)	ΔE_v (eV)
10 Å LaAlO ₃ / <i>n</i> -Si	1.75 ± 0.2	3.35 ± 0.1
10 Å LaAlO ₃ / <i>p</i> -Si	1.93 ± 0.2	3.17 ± 0.1
20 Å LaAlO ₃ / <i>p</i> -Si	1.99 ± 0.2	3.11 ± 0.1
40 Å LaAlO ₃ / <i>n</i> -Si	1.76 ± 0.2	3.34 ± 0.1
40 Å LaAlO ₃ / <i>p</i> -Si	1.88 ± 0.2	3.22 ± 0.1

Biosensors Based on Conductive Nanomaterials

Y Lin,^(a) J Wang,^(b) Y Tu,^(c) ZF Ren,^(c) and J Liu^(d)

(a) Pacific Northwest National Laboratory, Richland, Washington

(b) New Mexico State University, Las Cruces, New Mexico

(c) Boston College, Chestnut Hill, Massachusetts

(d) Sandia National Laboratories, Albuquerque, New Mexico

The key issues for development of electrochemical sensors and biosensors for environmental and biomedical monitoring are long-term stability, sensitivity, and response time. Recent advances in nanotechnology offer great potential for the construction of next-generation chemical sensor and biosensor devices. Recently, researchers have developed electrochemical sensors and biosensors based on conducting polymer nanowires and carbon nanotubes.

The first nanostructured conductive material was made by aligning nanowires of a conducting polymer, polyaniline (PANI). Researchers developed a templateless approach for electrosynthesis by conducting polymer nanowires on platinum and gold electrodes. Nanoparticles of an electron transfer mediator, iron (III) hexacyanoferrate (FeHCF), were successfully deposited into the nanowire matrix by an *in situ* electrodeposition method. The properties of the nanocomposite materials were induced by the combination of a nanoporous-conducting polymer and a mixed valence compound. The nanoporous PANI film has an extremely high-surface area and provides excellent support for uniform dispersion of FeHCF particles in the third dimension. The high-surface area of nanoporous PANI films can also increase the loading capacity for FeHCF particles, which leads to high sensitivity in chemical and biological sensing applications. The usefulness of the nanocomposite materials has been demonstrated with an electrochemical sensor device for H₂O₂, the detection of which is widely investigated for enzyme-based biosensors.

Researchers have also investigated another conductive nanomaterial for biosensor development—carbon nanotube thin films that were immobilized on an electrode surface. Carbon nanotube is an attractive material for the development of biosensors because of its capability to provide strong electrocatalytic activity and minimize surface fouling of the sensors. Biosensors from two fabrication regimes have been investigated: (1) the co-immobilization of carbon nanotubes and enzymes on electrode surfaces, and (2) the growth of controlled-density-aligned carbon nanotubes for the fabrication of nanoelectrode arrays. In the first regime, the carbon nanotubes are either dispersed in solvents (e.g., sulfuric acid,

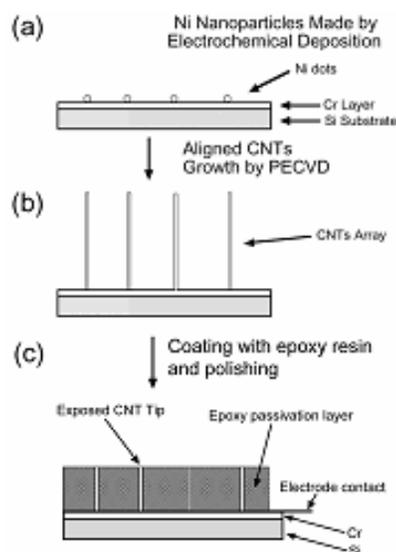


Figure 7. Fabrication scheme of a low-site-density-aligned carbon nanotube nanoelectrode array.

dimethylformamide, dissolved in Nafion solution for electrode coating, or mixed with Teflon as an electrode material for reagentless biosensors). In the second regime, the nanoelectrode arrays consisting of millions of vertically aligned carbon nanotubes, each acting as an individual electrode, were fabricated through a non-lithographic method (Figure 7). Researchers demonstrate the capability of CNTs to promote the oxidation/reduction (redox) reactions of hydrogen peroxide and nicotinamide adenine dinucleotide, which are involved in a wide range of amperometric biosensors associated with oxidase and dehydrogenase enzymes, respectively. With the development of electrocatalytic properties of carbon nanotubes, carbon nanotube-based biosensors have now been developed for glucose, nerve agents, and alcohol.

Damage Accumulation and Amorphization in Samarium Titanate Pyrochlore

Y Zhang,^(a) V Shutthanandan,^(a) R Devanathan,^(b) S Thevuthasan,^(a) DE McCready,^(a) JS Young,^(a) and WJ Weber^(b)

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

(b) Pacific Northwest National Laboratory, Richland, Washington

Materials of composition $A_2B_2O_7$ with the pyrochlore structure have remarkable elemental versatility, which makes these materials of considerable interest for the immobilization of actinide-rich nuclear waste. As a result of alpha decay, actinide-bearing phases will be subjected to considerable self-radiation damage. Radiation damage from alpha decay can result in amorphization, macroscopic swelling, and order-of-magnitude increases in dissolution rates, and these structural changes significantly affect the long-term performance of nuclear waste forms.

Recently, irradiation with gold ions was used to simulate alpha-recoil damage in samarium titanate pyrochlore ($Sm_2Ti_2O_7$) single crystals using EMSL's 3.0 MV tandem accelerator facility. The irradiation-induced defects are, for the first time, quantitatively characterized by channeling Rutherford backscattering spectrometry to achieve a better understanding of damage accumulation processes, which is essential to predict long-term performance of $A_2B_2O_7$ pyrochlores for the immobilization of actinides.

Damage accumulation under 1.0

MeV Au^{2+} irradiation at 170, 300, and 700 K is shown in Figure 8. The results indicate that the atomic disorder increases nonlinearly with dose, which is described well by a disorder accumulation model. Based on the fit to the disorder accumulation model, defect-stimulated

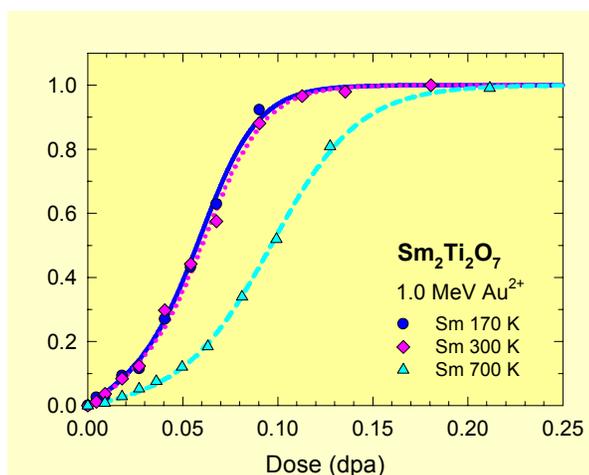


Figure 8. Relative samarium disorder at the damage peak as a function of dose for $Sm_2Ti_2O_7$ irradiated by 1.0 MeV Au^{2+} at 170, 300, and 700 K.

amorphization is a primary mechanism leading to amorphization in $\text{Sm}_2\text{Ti}_2\text{O}_7$.

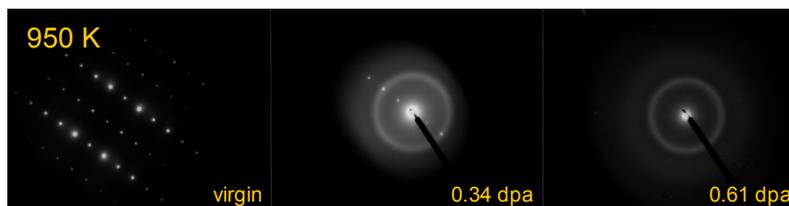


Figure 9. Diffraction patterns of $\text{Sm}_2\text{Ti}_2\text{O}_7$ irradiated with 0.6 MeV Bi^+ at 950 K. (a) Original, (b) 0.34 dpa, (c) 0.61 dpa.

The critical dose for amorphization in $\text{Sm}_2\text{Ti}_2\text{O}_7$ under 0.6 MeV Bi^+ irradiation was studied by *in situ* transmission electron microscopy (TEM) over a temperature range of 30 to 950 K. The Selected Area Electron Diffraction (SAED) patterns obtained from samples irradiated at 950 K are shown in Figure 9, which is representative of the general amorphization behavior observed at lower temperature irradiations. With increasing dose, the intense diffraction spots begin to fade, and amorphous halos appear in the SAED patterns. The pyrochlore crystal structure, as shown by the diffraction pattern, gradually amorphizes, all the diffraction spots vanish, and only the amorphous halos remain.

The critical dose for amorphization in $\text{Sm}_2\text{Ti}_2\text{O}_7$ under irradiation with 1.0 MeV Au^{2+} and 0.6 MeV Bi^+ is shown in Figure 10 as a function of temperature. Also included are the TEM results for $\text{Gd}_2\text{Ti}_2\text{O}_7$ irradiated with 0.6 MeV Bi^+ and due to alpha decay. Despite the six orders of magnitude difference in damage rates, the good agreement between the amorphization doses in $\text{Sm}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Ti}_2\text{O}_7$ under heavy ion irradiation and in $\text{Gd}_2\text{Ti}_2\text{O}_7$ due to ^{244}Cm decay indicate that amorphization due to heavy-ion energy deposition is relatively independent of dose rate at about room temperature. As a result, the model of damage accumulation and amorphization under heavy-ion irradiation in rare-earth titanates can be used to assess the impact of alpha-decay events on long-term performance.

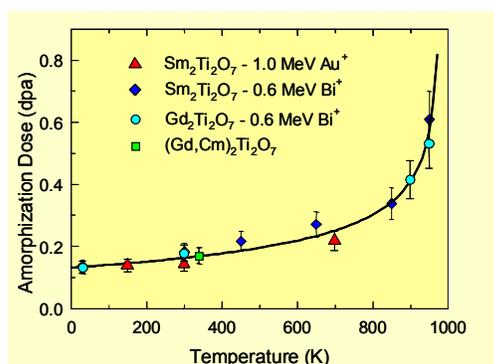


Figure 10. Critical dose for amorphization of $\text{Sm}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Ti}_2\text{O}_7$ irradiated by 1.0 MeV Au^{2+} , and 0.6 MeV Bi^+ . Also included are results for amorphization in $\text{Gd}_2\text{Ti}_2\text{O}_7$ doped with 3 wt% ^{244}Cm .

Subsurface Multifluid Flow and Multicomponent Reactive Transport: Characterization of Processes and Properties

SB Yabusaki,^(a) MK White,^(a) DH Bacon,^(a) VL Freedman,^(a) PC Lichtner,^(b) AJ Valocchi,^(c) SL Bryant,^(d) T Arbogast,^(d) M Wheeler,^(d) RJ Lenhard,^(e) PM Jardine,^(f) JC Parker,^(f) JP Gwo,^(g) K Pruess,^(h) and CI Steefel⁽ⁱ⁾

(a) Pacific Northwest National Laboratory, Richland, Washington

(b) Los Alamos National Laboratory, Los Alamos, New Mexico

(c) University of Illinois, Urbana, Illinois

(d) University of Texas, Austin, Texas

(e) Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho

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

(g) University of Maryland, College Park, Maryland

(h) Lawrence Berkeley National Laboratory, Berkeley, California

(i) Lawrence Livermore National Laboratory, Livermore, California

The cleanup of sites, such as legacy waste sites remaining from nuclear production, involves multiple physical and chemical processes with complex mixtures in strongly heterogeneous subsurface materials—all which make direct observation difficult. Computer modeling and simulation of contaminant behavior to accurately represent those processes at the field scale would enable the development of more efficient, cost-effective cleanup engineering strategies with less risk to biological receptors.

This project targets the characterization of subsurface processes and properties in multidimensional porous media as the unifying theme. The goal is to develop mechanistic process model representations and parameterizations that lead to enhanced understanding and scientifically defensible predictions of subsurface behavior. Long-term predictions of contaminant fate are critical to the management of the DOE missions of cleanup and long-term stewardship.

The work scope for this project addresses multidimensional laboratory and field experiments as well as site-specific, problem-driven site characterization, including history matching. A common theme for the simulations is the use of large numbers of grid cells (~105 to 107) to resolve multiple scales of subsurface heterogeneity. An important aspect of supporting these activities will be the testing and evaluation of parallel programming tools, debugging environments, and visualization software.

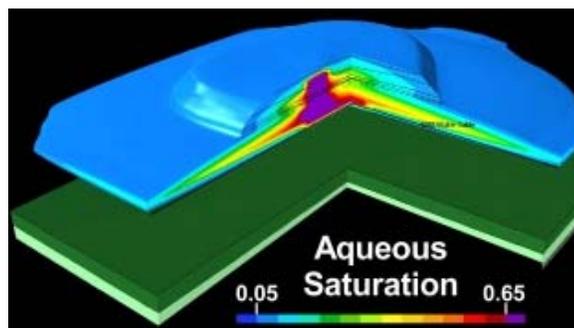


Figure 11. Simulation of the historical migration of carbon tetrachloride released from the Z-9 Crib in the variably saturated sediments of the Hanford Vadose zone.

A new constitutive theory for the migration of spreading and nonspreading, nonaqueous phase liquids through the Vadose zone was incorporated into the STOMP multifluid simulator and successfully validated. The model is currently being used to reconstruct the historical migration of carbon tetrachloride in variably saturated Vadose zone sediments on the Hanford Site (Figure 11).

A hierarchical parallel job distribution environment designed for parameter estimation and uncertainty analysis was developed using the Condor-G workload management framework for networked workstations and the Globus grid computing toolkit. The environment enables desktop submission and control of massive numbers of forward model simulations required for uncertainty analyses and inverse modeling with the flexibility of using local pools of workstations or high-end computing platforms on the national DOE Science Grid.

New capabilities were developed for the parallel Fortran Preprocessor (FP), which generates parallel code from a standard Fortran-90 source: 1) diagnostic feedback and consistency checking for distributed and shared arrays; 2) a utility to identify where results from the serial code differ from the generated parallel code; and 3) hierarchical communication that exploits on-node shared memory on symmetrical multiprocessing architectures. FP enabled the successful port of the STOMP and CRUNCH simulators to an entirely new 64-bit architecture operating system and compiler without modification of the source code.

Extension of Proteomic Technology to Study Brain-Related Diseases and to Produce a 3-D Image Map of Protein Expression throughout the Brain

RC Barry,^(a) HM Mottaz,^(b) EA Livesay,^(a) DG Camp II,^(a) RD Smith,^(a) DM Sforza,^(c) DJ Smith,^(c)

(a) Pacific Northwest National Laboratory, Richland, Washington

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

(c) University of California, Los Angeles, California

Researchers from the University of California, Los Angeles, EMSL, and PNNL are developing the first integrated three-dimensional model of the transcriptome and proteome constructs of the mouse brain in order to reveal the expression patterns of mRNA and proteins, respectively, throughout the normal brain and to ultimately compare the expression patterns of normal regions to regions apparently damaged from disease, drug abuse, or other trauma. A two-fold strategy is currently being used to (1) systematically map the protein and mRNA expression levels in spatially registered 1-mm³ volume elements (known as voxels, see Figure 12), and (2) investigate the regulation of mRNA and proteins in brain regions known to be specifically affected by certain diseases. Our initial pilot study for brain disease research will focus on methamphetamine-induced brain damage, which produces physiological effects similar to Parkinson's Disease in mice and primarily damages the striatum of the brain. We will seek to identify and quantify the differential expression of proteins within the damaged striatum, as compared to a healthy striatum, and establish a list of proteins that are most intimately associated with Parkinson's Disease-type symptoms.

In order to quantitatively map protein expression levels within voxels (samples containing less than 50 µg of tissue), efficient protein extraction procedures from lipid-laden tissues are being developed. The high-resolution chromatographic separations are being refined to analyze less than 5 µg of extracted protein by using smaller-diameter columns and higher pressures (15-30 µm, 10 to 20,000 psi), optimizing the Fourier-transform-ion cyclotron resonance mass spectrometers for maximum sensitivity, and developing an automated high-throughput nanoscale sample-handling platform to process the approximately 600 voxels obtained from a single mouse brain.

Recently, several different protein extraction protocols for brain tissue were evaluated, and we have confidently identified 863 proteins using automated mass spectral analysis software and very strict assignment rules (Table 2). This is the most extensive list of isolated and

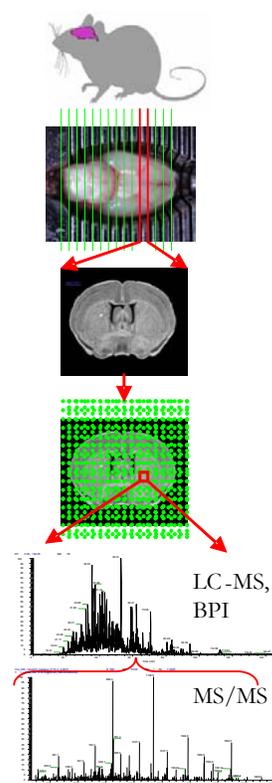


Figure 12. Mechanical preparation of voxels and mass spectrometric analysis.

identified brain proteins that we are aware of, and contains twice as many as previously reported in the literature by two-dimensional gel electrophoresis approaches. Two detergent-based protocols (one an in-house mixture, DC, and the other a commercially available reagent, RG), were tested for their ability to extract proteins from lipid-laden tissue and their potential suitability for automated sample handling. These two methods were compared with a more laborious technique that requires homogenizing the sample using glass beads, using ultracentrifugation to separate the water-soluble (WS) fraction from water-insoluble fraction (WI), solubilizing the WI pellet, and then subjecting each fraction to trypsin proteolysis. The advantage of the subfractionation scheme is the ability to reduce sample complexity and gain information as to the subcellular location of proteins. The WS fraction (442 unique proteins^(a)) typically contains cytosolic and loosely associated peripheral membrane proteins, while the WI fraction (283 unique proteins^(a)) contains mostly membrane-associated proteins. The DC^(b) and RG^(c) methods resulted in 265 and 264 unique proteins, respectively. Thus, by comparing the overlap of proteins identified from using our detergent-based protocols with those from the WS and WI fractions, we are able to evaluate the types of proteins extracted using DC or RG reagents (Table 2). Both detergents performed equally well, although the brain material was much more completely solubilized when using the DC solution as compared to the RG solution. For automation purposes, both samples would require a 14,000 x g spin before performing liquid chromatography-mass spectrometry analysis.

Table 2. Comparison of Methods for Protein Extraction and Identifications for Mouse Brain Tissue.

Overlap					
WS/WI ^(a)	DC ^(b) /WS	RG ^(c) /WS	DC/WI	RG/WI	DC/RG
36%	46%	57%	57%	56%	44%
Comparison to Literature					
Method	Ultra-high resolution reversed-phase liquid chromatography and ion trap mass spectrometry	High-resolution 2-DE	High-resolution 2-DE	High-resolution 2-DE	High-resolution 2-DE
Unique Proteins	863	437	210	180	90

(a) WS = water-soluble, WI = water-insoluble. For WS and WI: 100 mg wet wt, add 500 μ L of 100 mM AmBic, homogenize with glass beads, 100K x g spin 15 min. S.N = WS. For WI: to pellet add 100 μ L 7M urea, 2M thiourea, 1% CHAPS, in 50 mM AmBic, pH 7.8, 10 mM DTT, dilute 10 fold add excess trypsin (total vol. 1.56 mL)

(b) DC Buffer: Detergent and Chaotrope Buffer: 7M urea, 2M thiourea, 3% CHAPS, 1% ASB-14, 4 mM TCEP, 4 mM TBP, 50 mM tris HCl or AmBic, pH 7.8. For DC samples: 10 mg wet wt brain +100 μ L DC, vortex 30 sec., bath sonicate 30 min., let stand 1h, dilute 4-fold, add trypsin incubate 37°C 12-16 h

(c) RG: 0.2% Rapid Gest (available from Waters Corp) 10 mM DTT vortex 30 sec., bath sonicate 30 min., let stand 1h, dilute 2-fold, add trypsin, incubate 37°C 12-16 h.

Currently, we are investigating ways to extract more biomolecules from a given voxel while developing a more automation-friendly protein extraction technique. In particular, we are testing methods to subfractionate the brain material into an aqueous layer (containing peptides, RNA, and aqueous soluble small molecule metabolites) and an organic layer (containing lipids and hydrophobic metabolites), with the interphase containing DNA; thereby establishing an information-rich technique for a more complete analysis of each voxel.

Models for Radiation-Induced Release of Cytokines by Autocrine-Cell Systems: Implications for Bystander Effects

J Miller,^(a) F Zheng,^(a) H Resat,^(b) L Opresko,^(b) DL Springer,^(b) and HS Wiley^(b)

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

(b) Pacific Northwest National Laboratory, Richland, Washington

Experiments performed at the Gray Cancer Institute using a charged-particle microbeam and a soft X-ray microprobe have shown that levels of bystander-mediated cell killing are primarily determined by the amount of energy deposited in single cells rather than the number of targeted cells. We have proposed that autocrine processes—where capture of a ligand on a cell-surface receptor stimulates shedding of the same ligand—are the mechanism for this type of bystander effect. Community effects are a well-established feature of cellular systems when the spatial range of autocrine signals is on the micrometer scale (Wiley et al. 2003). Under these conditions, signals from the perturbation of a single cell can be quickly relayed to all of the cells in a high-density population. We are developing models that integrate data from a variety of sources to address the question of whether low doses of ionizing radiation stimulate this type of cell-to-cell communication. In this research, we focus on the critical issue of the magnitude of shedding induced in cells that receive energy directly from low-linear energy transfer radiation.

TGF α , an autocrine ligand of the epidermal growth factor receptor (EGFR), has been shown to mediate secondary activation of EGFR and downstream mitogen-activated protein kinase (MAPK) and c-Jun NH₂-terminal kinase (JNK) signaling pathways (Dent et al. 1999). Data on MAPK activation by 2 Gy of gamma irradiation delivered at a dose rate of 1.1 Gy/min are shown in Figure 13. Like Shvartsman et al. (2002), our models predicted secondary MAPK-activation kinetics more rapid than that observed by Dent et al. (1999) when the rate of protease activation was assumed to be proportional to the instantaneous prompt MAPK activity. The result shown by the solid curve in Figure 13 is based on the hypothesis that the rate of protease activation is proportional to the integral of the prompt MAPK activity multiplied by a Gaussian weighting function that introduces a time delay of approximately two hours. The biological basis for this mode of coupling MAPK activity to protease activation is unclear; however, we note that a dependence of the specificity of receptor tyrosine

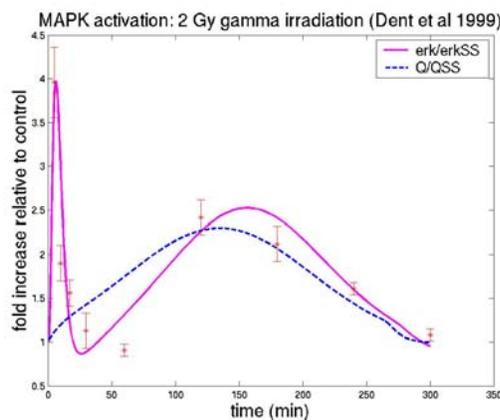


Figure 13. Kinetics of MAPK activation by 2 Gy of gamma irradiation.

kinase signaling on the duration of extracellular regulated kinase activation is well established (Marshall 1995). The dashed curve in Figure 13 shows the magnitude and kinetics of shedding predicted by this model.

Direct observation of shedding under autocrine conditions is difficult due to the low probability that shed proteins escape into the bulk extracellular medium; hence, the use of antibodies that facilitate escape by blocking receptors is a common experimental practice. Data on shedding of EGF obtained in Opresko's laboratory by this method are shown in Figure 14 by the diamonds and asterisks. The solid curves show our model predictions under blocking conditions based on the same assumptions used to model the TGF α -mediated MAPK activation observed by Dent et al. (1999) at higher doses. The fit to data on shedding by unirradiated human mammary epithelial cells/human conjunctival fibroblasts cells (solid curve) was obtained with a constant shedding rate of 37 EGF molecules per minute. Shedding induced in the same cell line by 2.5 cGy of gamma irradiation was explained by a time-dependent release rate with a shape similar to the dashed curve in Figure 13 and with a maximum value 1.8 times the shedding rate of unirradiated control cells. Whether shedding of this

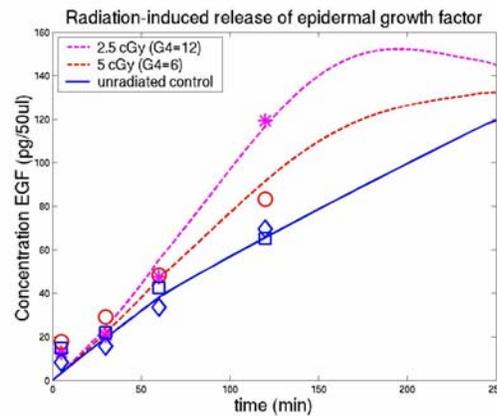


Figure 14. Radiation-induced shedding of EGF by 2.5 and 5 cGy of gamma irradiation.

magnitude by a hit cell can induce a community response among bystanders will depend on several factors, which include ligand diffusivity, ligand-receptor affinity, steady-state level of free receptors, and cell plating density. Simulation techniques to investigate the interplay of these factors are under development.

Citations

Dent P, DB Reardon, JS Park, G Bowers, C Logsdon, K Valerie, and R Schmidt-Ullrich. 1999. "Radiation-Induced Release of Transforming Growth Factor α Activates the Epidermal Growth Factor Receptor and Mitogen-Activated Protein Kinase Pathway in Carcinoma Cells, Leading to Increased Proliferation and Protection from Radiation-induced Cell Death." *Molecular Biology of the Cell* 10(8):2493-2506.

Marshall CJ. 1995. "Specificity of Receptor Tyrosine Kinase Signaling: Transient versus Sustained Extracellular Signal-Regulated Kinase Activation." *Cell* 80:179-85.

Shvartsman SY, MP Hagan, A Yacoub, P Dent, HS Wiley, and DA Lauffenburger. 2002. "Autocrine Loops with Positive Feedback Enable Context-Dependent Cell Signaling." *American Journal of Physiology, Cell Physiology* 282(3):C545-559.

Wiley HS, SY Shvartsman, and DA Lauffenburger. 2003. "Computational Modeling of the EGF-Receptor System: A Paradigm for Systems Biology." *Trends in Cell Biology* 13(1):43-50.

Relativistic Quantum Chemistry Studies of the Electronic Structures and Photoelectron Spectra of Negatively Charged Transition-Metal Complexes

J Li,^(a) K Boggavarapu,^(b) and LS Wang^(b)

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

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

The central theme of this project is to elucidate electronic and geometrical features of various atomic clusters identified by anion photoelectron spectroscopy experiments. Theoretical investigations were performed on four topics in close collaboration with researchers from Washington State University-Tri-Cities and EMSL. The following is a brief summary.

An Unusual and Exceptionally Stable Au₂₀ Tetrahedral Nanocluster

Experimental studies reveal that a series of naked gold clusters can be formed with Au₂₀ being exceptionally stable and having a highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) energy gap around 1.8 eV. Through numerous structural searches and theoretical modeling of the electronic properties, we discover that Au₂₀ possesses an unusual tetrahedral pyramid structure (Figure 15). The calculated HOMO-LUMO gap, electron detachment energies, and excitation energies are in excellent agreement with those measured experimentally. We also find that this nanocluster has remarkably large second-order optical nonlinearity, and its materials are expected to have great potentials in catalysis and optoelectric devices.

Observation and Identification of Icosahedral Mo@Au₁₂ and W@Au₁₂ Molecules

By using relativistic Density Functional Theory (DFT) calculations, we fully explored the electronic structures and energetics of the icosahedral, octahedral, and cubo-octahedral structures of W/Mo-Au₁₂ clusters observed by Wang's group. The calculated icosahedral structures (Figure 16) of these clusters have the lowest energy among their isomers and the theoretically simulated photoelectron spectra are in good agreement with the experimental results. These clusters are thus confirmed to possess an

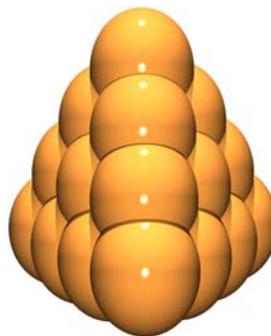


Figure 15. Optimized tetrahedral Au₂₀ structure.

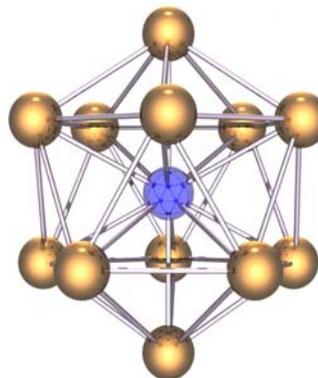


Figure 16. The structure of icosahedral W@Au₁₂.

endohedral icosahedral structure with an extremely stable electronic configuration, as previously predicted by Pyykko (2002). This work is the first confirmation of icosahedral gold clusters.

Hydrocarbon Analogs of Boron Clusters

Using density functional geometry optimizations, we have determined the geometry structures of a series of boron clusters B_x ($x = 10 - 16$) discovered in Wang's group. In contrast to the elemental boron and boron compounds where highly symmetric icosahedral structure dominates, small boron clusters are found to have quasi-planar structures and exhibit aromaticity and antiaromaticity according to the famous Hückel rule. Our calculations revealed that the aromatic boron clusters possess circular shapes, whereas antiaromatic ones are elongated, analogous to structural distortions of antiaromatic hydrocarbons. These planar boron clusters are the only series of molecules other than the hydrocarbons to exhibit size-dependent aromatic and antiaromatic characters in chemistry.

Structure and Bonding in $Fe-S_n^-$ ($n = 1-6$) clusters

We have undertaken computational study on mono-iron-poly-sulfur systems that are essential in understanding electronic structures of iron-sulfur proteins. With experimental photoelectron spectroscopic results as guidelines we explored various geometrical and electronic states of $Fe-S_n^-$ clusters by DFT methods, and good agreement has been reached between the computed and experimental electron affinities. We discover that iron is not oxidized beyond its favorite +2 or +3 oxidation states as found in iron-sulfur proteins and the geometry and electronic structure evolution of FeS_n^- systems is quite different from the corresponding FeO_n^- species.

Citation

Pyykkö P. 2002. "Relativity, Gold, Closed-Shell Interactions, and $CsAu \cdot NH_3$ " *Angewandte Chemie International Edition* 41(19):3573-3578.

High-Resolution Infrared Spectroscopy Laboratory is Major Contributor to Special Spectroscopy Journal Issue on HITRAN Database

RL Sams,^(a) TA Blake,^(b) and SW Sharpe^(a)

(a) Pacific Northwest National Laboratory, Richland, Washington

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

A special issue of the *Journal of Quantitative Spectroscopy and Radiative Transfer* was commissioned to report on the status, to our best knowledge, of the quantitative molecular spectroscopic data on atmospheric constituents. This special issue is devoted to both the status of, and the continuing research that has been contributing to, the compilation of spectroscopic data known as the High resolution TRANsmission (HITRAN) spectroscopic database. The HITRAN (<http://www.hitran.com>) compilation has come to be considered globally as the source for the spectroscopic properties of important atmospheric constituents, as shown in Figure 17. It serves as a valuable input to transmittance and radiative-transfer modeling codes. Thus, it is vital to the remote-sensing applications of the atmosphere as well as to the models devised to gauge global warming. The compilation has several segments. The major part of the database consists of individual spectral line parameters of atmospheric molecules. The other parts consist of absorption cross-sections for molecules with very dense spectral features, aerosol refractive indices, ultraviolet line-by-line parameters and absorption cross-sections, and the associated “management software” for the database. Phenomena that are easily parametrized in acceptable forms for modeling codes, such as collision-induced absorption, line coupling, and similar spectroscopic phenomena, are under consideration for future editions. In addition, more molecular entities, bands, basic spectroscopic quantities, and documentation will be incorporated.

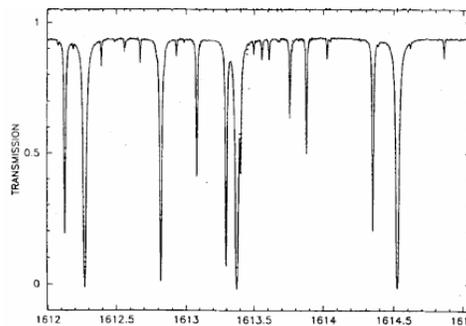


Figure 17. High-resolution infrared spectrum of gas phase NH_3 .

In the special issue, six of the 30 articles are based on experimental data obtained in the High-Resolution Infrared Spectroscopy Laboratory. These six articles, written in collaboration with more than 40 external user/collaborators, appear in the *Journal of Quantitative Spectroscopy and Radiative Transfer* and are listed below.

Citations

Brown LR, DC Benner, JP Champion, VM Devi, L Fejard, RR Gamache, T Gabard, JC Hilico, B Lavorel, M Loete, GC Mellau, A Nikitin, AS Pine, A Predoi-Cross, CP Rinsland, O Robert, RL Sams, MAH Smith, SA Tashkun, and VG Tyuterev. 2003.

“Methane Line Parameters in HITRAN.” *Journal of Quantitative Spectroscopy and Radiative Transfer* 82(1-4):219-238.

Chackerian C, SW Sharpe, and TA Blake. 2003. “Anhydrous Nitric Acid Integrated Absorption Cross Sections: 820-5300 cm^{-1} .” *Journal of Quantitative Spectroscopy and Radiative Transfer* 82(1-4):429-441.

Devi VM, DC Benner, MAH Smith, CP Rinsland, SW Sharpe, and RL Sams. 2003. “A Multispectrum Analysis of the ν_1 Band of $\text{H}^{12}\text{C}^{14}\text{N}$: Part I. Intensities, Self-Broadening and Self-Shift Coefficients.” *Journal of Quantitative Spectroscopy and Radiative Transfer* 82(1-4):319-341.

Kleiner I, G Tarrago, C Cottaz, L Sagui, LR Brown, RL Poynter, HM Pickett, P Chen, JC Pearson, RL Sams, GA Blake, S Matsuura, V Nemtchinov, P Varanasi, L Fusina, and G Di Lonardo. 2003. “ NH_3 and PH_3 Line Parameters: The 2000 HITRAN Update and New Results.” *Journal of Quantitative Spectroscopy and Radiative Transfer* 82(1-4):293-312.

Rinsland CP, VM Devi, MAH Smith, DC Benner, SW Sharpe, and RL Sams. 2003. “A Multispectrum Analysis of the ν_1 Band of $\text{H}^{12}\text{C}^{14}\text{N}$: Part II. Air- and N_2 -Broadening, Shifts and Their Temperature Dependences.” *Journal of Quantitative Spectroscopy and Radiative Transfer* 82(1-4):343-362.

Rinsland CP, SW Sharpe, and RL Sams. 2003. “Temperature-Dependent Absorption Cross-Sections in the Thermal Infrared Bands of SF_5CF_3 .” *Journal of Quantitative Spectroscopy and Radiative Transfer* 82(1-4):483-490.

Probing Conformational Changes of Gramicidin Ion Channels by Single-Molecule Patch-Clamp Fluorescence Microscopy

GS Harms,^(a) G Orr,^(a) M Montal,^(b) BD Thrall,^(a) SD Colson,^(a) and HP Lu^(a)

(a) Pacific Northwest National Laboratory, Richland, Washington

(b) University of California at San Diego, La Jolla, California

Complex conformational changes influence and regulate the dynamics of ion channels. Such conformational changes are stochastic and often inhomogeneous, which makes it extremely difficult, if not impossible, to characterize them by ensemble-averaged experiments or by single-channel recordings of the electric current that report the open-closed events but do not specifically probe the associated conformational changes. In this work, researchers at PNNL and the University of California, San Diego report on studies of ion channel conformational changes using a new approach, patch-clamp fluorescence microscopy (PCFM), which simultaneously combines single-molecule fluorescence spectroscopy and single-channel current recordings to probe the open-closed transitions and the conformational dynamics of individual ion channels (Figure 18). They demonstrate PCFM by measuring gramicidin ion channel conformational changes in a lipid bilayer formed at a patch-clamp micropipette tip under a buffer solution. By measuring single-pair fluorescence resonance energy transfer and fluorescence self-quenching from dye-labeled gramicidin channels, it was observed that the efficiency of single-pair fluorescence resonance energy transfer and self-quenching is widely distributed, which reflects a broad distribution of conformations. These results strongly suggest a hitherto undetectable correlation between the multiple conformational states of the gramicidin channel and its closed and open states in a lipid bilayer.

The new single-molecule experimental technique, PCFM, provides a novel approach for studying ion channel conformational dynamics and mechanisms. This technique should be applicable for the direct study of ion channel proteins in living cells and opens the door to a fundamental understanding of ion transport in these systems. Details on this exciting research can be found in Harms et al. 2003.

Citation

Harms GS, G Orr, M Montal, BD Thrall, SD Colson, and HP Lu. 2003. "Probing Conformational Changes of Gramicidin Ion Channels by Single-Molecule Patch-Clamp Fluorescence Microscopy." *Biophysical Journal* 85(3):1826-1838.

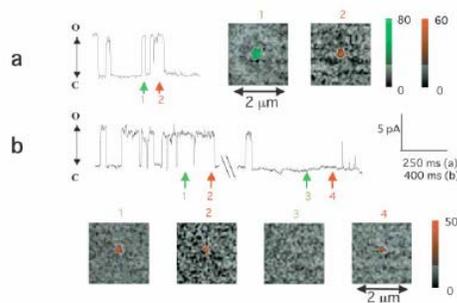


Figure 18. Concurrent patch clamp and fluorescence microscopy measurement of single TMR/Cy5-gramicidin heterodimer ion channels. The combined use of the two techniques allows for the determination of the ion transport mechanism.

Computational Grand Challenge Allocations for FY04

The Hewlett-Packard supercomputer, ordered in April 2002 and operational in August 2003, is installed in the Molecular Science Computing Facility (MSCF). Large blocks of computing time are granted to multi-institutional research teams on a competitive proposal basis. Fifteen MSCF Computational Grand Challenge projects were awarded over 8 million CPU hours, 81% percent of the available time. The remaining time will be allocated to users as requests are made through the year. Ten new projects started and five are continuing the third year of their research. The users come from more than 40 universities and eight government research facilities, such as the University of Houston, Emory University, Columbia University, NOAA, and the National Center for Atmospheric Research. Funding for individuals performing the research come from many different sources that include DOE, NIH, NSF, DoD, NSF, NASA, academia, and industry. They are performing research in scientific topics such as chemical transformations for catalyst design, the physics and chemistry of biochips, synthesis and reactivity of nanomaterials, dynamics of damaged DNA and a new approach to atmospheric global climate models. Full details will be available on the MSCF web page (<http://mscf.emsl.pnl.gov>). The ten new projects and their PI's include:

- Superparameterization: A New Paradigm for Climate Modeling, Thomas P. Ackerman, Pacific Northwest National Laboratory, Richland, Washington
- Molecular Computational Studies in Environmental Chemistry, Geochemistry, and Biogeochemistry, Eric J. Bylaska, Pacific Northwest National Laboratory, Richland, Washington
- Nanostructure Formation, Aggregation, and Reactivity, Keiji Morokuma, Emory University, Atlanta, Georgia
- Reliable Electronic Structure Prediction of Molecular Properties, David A. Dixon Pacific Northwest National Laboratory, Richland, Washington
- Direct Dynamics Simulations: From Molecules Macromolecules and Condensed Phases, William L. Hase, Wayne State University, Detroit, Michigan
- Computational Design of Catalysts: The Control of Chemical Transformation, Maciej S. Gutowski, Pacific Northwest National Laboratory, Richland, Washington
- Multiscale Modeling of Biochip Systems, B. Montgomery Pettitt, University of Houston, Houston, Texas
- Complex Enzymatic Reactions Studied by Molecular Modeling and Electronic Structure Calculation, TP Straatsma, Pacific Northwest National Laboratory, Richland, Washington
- Multifluid Flow and Multicomponent Reactive Transport in Heterogeneous Subsurface Systems, Steve Yabusaki, Pacific Northwest National Laboratory, Richland, Washington
- Image Processing, Modeling and Simulation of Complex Biological Systems Using Volume Filling and Boundary Fitted Mesh Based Methods, Harold E. Trease, Pacific Northwest National Laboratory, Richland, Washington

Awards and Recognition

Marianne Resat, W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington and Lee Opresko, Pacific Northwest National Laboratory, Richland, Washington, were awarded a research grant worth over \$1M entitled "Mechanisms of Three-Dimensional Intercellular Signaling in Mammary Epithelial Cells in Response to Low Dose, Low LET Radiation; Implications for the Radiation-Induced Bystander Effect." Their project will apply novel three-dimensional imaging technologies toward understanding the response of higher order cellular structures to low doses of radiation. The Low-Dose Radiation Program is a highly competitive program, and this award is indicative of the outstanding quality of their proposal. Most importantly, the success of this proposal provides an important demonstration of how basic research in systems biology combined with development of novel technologies can be translated to address critical DOE mission needs. The DOE Low-Dose Radiation Program is the primary human biological research mission for DOE's Office of Science. As such, success in applying new technologies and approaches in support of the Low-Dose Radiation Program is critical for the successful growth of systems biology research at PNNL.

Steve Tait, University of Washington, Seattle, Washington, recently won the "Best Graduate Student Poster" at the Pacific Northwest Chapter of the American Vacuum Society annual meeting held September 17-18, 2003 in Troutdale, Oregon. Steve's poster, "Adsorption Energies of Small Alkane Molecules on MgO(100) and on Pd Nanoparticles on MgO by Temperature Programmed Desorption," was based on work conducted in EMSL's Molecular Beam Scattering and Dynamics Laboratory. The co-authors on the poster were PNNL researchers Zdenek Dohnálek and Bruce D. Kay, and Charles T. Campbell of the University of Washington. Steve will receive a \$1000 prize to be used to cover his expenses to attend the National American Vacuum Society Meeting to be held in Baltimore, Maryland, November 2-7, 2003.

Professional/Community Service

David W. Hoyt of EMSL's High-Field Magnetic Resonance Facility served as a panelist reviewing chemical research instrumentation grants for the National Science Foundation in Arlington, Virginia, on October 22 - 24, 2003.

Theresa Windus, from EMSL's Molecular Science Computing Facility, was selected to serve on the Editorial Board of the new *Journal of Computational and Theoretical Nanoscience*.

Major Facility Upgrades

Design and construction of the dual-energy gamma-radiation system and intermediate scale flow cell have been completed. The system—located in the Environmental Spectroscopy and Biogeochemistry Facility—will be used to nondestructively and noninvasively determine fluid saturation, porous medium bulk density, porosity, and salt concentrations values. In addition, the computer and software on the facility's fluorimeter were upgraded, and a laser excitation Nikon TE-2000 fluorescence microscope system has been purchased and installed. The latter system will be used to directly image uranium (VI) distribution in contaminated sediments, and *in situ* observation of the dissolution or sorption fluorescent contaminants in mineral solids.

The large supercomputer in the Molecular Science Computing Facility (MSCF) was upgraded in August. During the upgrade, the QSnet II/elan4 network hardware was installed, and software testing has begun. When fully operational, this network will allow shorter latencies in the node-to-node communications. It will also more than triple the communication bandwidth between nodes. This improvement in node-to-node communication will allow applications to scale better and run on larger numbers, thus decreasing the time to solution.

In addition, the MSCF core router was upgraded with a Catalyst 6500 Supervisor Engine 720. This engine integrates a high-performance 720 gigabits per second (Gbps) switch fabric with a new routing and forwarding engine, including a third-generation Policy Feature Card in a single module. The engine delivers the scalable-performance, intelligence, and broad selection of features for building modular, resilient, scalable, secure, multilayer switching solutions. Our switching backplane increased from 32 Gbps to 720 Gbps. This upgraded engine also allows MSCF Operations personnel to upgrade the network link to the EMSL core network to 20 Gbps once the EMSL core router has been upgraded. The operating system was also upgraded from CAT OS 8 to IOS 12, which will improve routing performance and significantly simplify management of the core router.

Laboratory-Directed Research and Development funds have been approved to explore the integration of local data processing into a cluster-based file system. This new approach to data processing will allow the file system to process and filter data as it is being written, reducing the quantity of data stored and the need for post-processing. A simple application of this concept is to process the data stream and report where specific sequences appear, such as a text string or even computer virus code.

The eventual goal is to provide a way for researchers to process the data being written to the archive on-the-fly as the data come off of a data collection device and are sent to the storage device. In this way, the unused portion of processor time on the storage servers can be used to analyze the data stored on the server and compute results.

A new ceiling-mounted digital video projection unit was installed in the MSCF Graphics & Visualization Laboratory (GVL). This new unit replaces the analog Electrohome 8500+ projector purchased in 1997. It is a high-performance stereo DLP projector, Mirage 2000, manufactured by Christie Electronics (Figure 19). The Mirage 2000 is the next-generation of stereoscopic digital projectors to revolutionize the virtual reality and simulation market. Based on high-resolution SXGA 3-chip DLP™ technology, the Mirage 2000 offers new levels of brightness and image clarity not previously available. At the heart of the Mirage 2000 are Christie-designed electronics that provide high bandwidth, frame rates, pixel and clock speeds resulting in the most advanced digital signal processing for all types of stereo images. This design employs dark interval adjustments (DIA™) control that enhances the overall stereo effect by fine-tuning the critical time between left and right fields.

It also features primary color adjustment control (PCA™), ensuring true color representation of all source images. The Mirage 2000's DMD technology is inherently faster than LCD and has the ability to synchronize the left and right fields required for stereo imaging without time lag, ghosting, or other artifacts - resulting in more accurate color reproduction and uniformity. Christie's advanced optical alignment technique, known as spatial light imaging construction (SLIC™), sets a new quality standard that guarantees optimum focus and convergence accuracy. With this proprietary process, the Mirage 2000 delivers the new industry standard in brightness, clarity and enhanced depth perspective - providing the ultimate in real time, real life projection simulations. User comments after unit was installed included "Woo, crystal clear and bright," "It sure beats the desktop InFocus projectors," and "Images seem to come out of the screen."

In addition, a new Apple G5 Macintosh (Figure 20) computer with high-resolution display was installed in the GVL in October. This new unit replaces the Apple G4 Mac purchased in 2000. The new unit is comprised of G5 Dual 2 GHz with 2GB SDRAM (PC3200), 2x250GB hard drives, ATI Radeon 9800 Pro Video Card, 56k V.92 internal modem, SuperDrive (DVD-R/CD-RW), Apple keyboard and mouse, running Mac OS X. The computer has a new Apple 23-inch HD Cinema display that supports 1920 x 1200 pixel resolution (Figure 21). User comments after system became operational and software installed include "Maya runs faster here than on the SGI," "Rendering, is like, super fast," and "Display is fantastic, I can't wait until I get one."



Figure 19. Mirage 2000 Video Projector



Figure 20. Apple G5 Macintosh Computer.



Figure 21. Apple 23-inch high-definition cinema display.

News Coverage

PNNL announced that the Laboratory has won a five-year, \$10.2 million grant from the National Institutes of Health to support a center for basic research in proteomics. (<http://www.eurekalert.org/doe/releases.php?topic=bio>) It is the largest NIH grant in the Department of Energy lab's 38-year history. The resource center is housed at the W.R. Wiley Environmental Molecular Sciences Laboratory, where capabilities include automated ultra-high resolution mass spectrometers and separations systems for rapid and extremely sensitive characterization of the complex protein groups of organisms. This was also covered in the October 16 issue of *Nature* in the "News in Brief" and other media.

HP UNVEILS WORLD'S FASTEST LINUX SUPERCOMPUTER (hpcwire Oct 24)
The world's largest Linux supercomputer - built on HP Integrity servers - is now fully operational at the U.S. Department of Energy's Pacific Northwest National Labs (PNNL). The 11.8 teraflop PNNL system is considered the nation's fastest non-military supercomputer and will enable scientists to both solve complex scientific problems faster and conduct more advanced scientific research. This system is the latest from HP, the leader in clustering and high-performance computing solutions.

Visitors and Users

Chemistry and Physics of Complex Systems Facility

- Massimo Bertino, University of Missouri-Rolla, Rolla, Missouri, gave the seminar "Fabrication of Nanostructures with Ionizing Radiation."
- Alan Finkelstein, Albert Einstein College of Medicine, Bronx, New York, gave the seminar "Protein Translocation Associated with Channel Gating."
- Masatake Haruta, Susumu Tsubota, and Masakazu Date, Research Institute for Green Technology, National Institute of Advanced Science and Technology, Tokyo, Japan, gave the seminar "Catalysis and Applications of Gold."
- Byung Kim, Sandia National Laboratories, Albuquerque, New Mexico, gave the seminar "Scanning Probe Microscopy on Bio-Active Surfaces and Organic Self-Assembly."
- Alan T. Maccarone, University of Colorado-Boulder, Boulder, Colorado, worked with Alan Joly and Doug Ray, Pacific Northwest National Laboratory, Richland, Washington, on research regarding organic water/air interfaces.
- Klaus Mueller and Peter Imrich, Stony Brook University, Stony Brook, New York, worked with Alla Zelenyuk, Pacific Northwest National Laboratory, Richland, Washington, on development of data analysis and visualization software, SpectraMiner.

- Joel H. Parks, Rowland Institute at Harvard, Cambridge, Massachusetts, gave the seminar "Fraying and Electron Autodetachment Dynamics of Trapped Gas Phase Oligonucleotides."
- Lai-Sheng Wang, Washington State University, Tri-Cities, Washington, continues to work in a joint appointment capacity with PNNL on the study of metal and metal-carbon mixed clusters. He brings with him a group of eight postdoctoral research fellows and graduate students to conduct his ongoing research.

Environmental Spectroscopy and Biogeochemistry Facility

- Paul S. Bagus, Texas A&M University, College Station, Texas, collaborated with Eugene Ilton, Pacific Northwest National Laboratory, Richland, Washington, to further develop a theoretical model for the X-ray photoelectron spectroscopy (XPS) of transition metals. A new near-degenerate configuration was shown to explain certain fine structures for the XPS of manganese.
- G.V. Gibbs, Virginia Polytechnic Institute, Blacksburg, Virginia, collaborated with Kevin Rosso, Pacific Northwest National Laboratory, Richland, Washington, to initiate two new series of *ab initio* calculations pertaining to mapping electron density distributions in Fe^{II}-bearing mineral phases and also in rhombohedral and prismatic faces of alpha quartz. For the latter, the Laplacian of the electron density distribution of optimized periodic and cluster surface representations will be analyzed for locations of nucleophilic and electrophilic attack to address issues of quartz dissolution mechanisms at an atomistic level.
- Peter Jaffe and John Komlos, Princeton University, Princeton, New Jersey, in collaboration with Ravi Kukkadapu, W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington, used Mössbauer spectroscopy to probe reductive transformation of iron in a shale-limestone saprolite containing Fe^{III} oxides and Fe^{II}/Fe^{III} phyllosilicates. This research will be useful in understanding the trace metal remediation in the reduced soils and sediments.

High-Field Magnetic Resonance Facility

- Cheryl Arrowsmith, University of Toronto, Toronto, Ontario, Canada, sent samples to be run on the 500-MHz, 600-MHz, and 750-MHz spectrometers for the study "Structural Proteomics: Annotating the Genome Using 3D Structure."
- Peter Brzovic, University of Washington, Seattle, Washington, used the 600-MHz spectrometer for "NMR Structural Investigations of BRCA1."
- Brian R. Cherry, Sandia National Laboratories, Albuquerque, New Mexico, used the 500-MHz wide bore spectrometer for the study "Investigating the Heterogeneity of Polymer Aging."

- Youjun Deng, Washington State University, Pullman, Washington, recently used the 400-MHz spectrometer for the study “Variable-temperature MAS NMR Spectroscopic Study of Incorporated and Sorbed ^{13}C s and ^{23}Na in Zeolitic Minerals.”
- Kathryn R. Ely and Klara Briknarova, The Burnham Institute, La Jolla, California, sent samples to be run on the 600-MHz spectrometer for the study of “Structural Characterization of Free and Fibronectin-Bound Anastellin.”
- Stephen Holbrook, Lawrence Berkeley National Laboratory and the University of California, Berkeley, California, sent samples to be run on the 600-MHz spectrometer for the study “Structural Biology of DNA Repair Proteins: The Nudix Protein Family from the Extremely Radiation-Resistant Bacterium *Deinococcus radiodurans*.”
- Evan Kantrowitz, Boston College, Chestnut Hill, Massachusetts, sent samples to be run on the 500-MHz wide bore and the 400-MHz spectrometers for the study “Probing the Mechanism of the Alkaline Phosphatase Reaction by ^{67}Zn and ^{25}Mg NMR.”
- Flemming Larsen, University of Copenhagen, Copenhagen, Denmark, sent samples to be run on the 800-MHz and 500-MHz wide bore spectrometers for the study “Separation of ^{47}Ti and ^{49}Ti Solid-State NMR Lineshapes from Crystalline and Glassy Materials by Static QCPMG Experiments.”
- Chongxuan Liu, Pacific Northwest National Laboratory, Richland, Washington, sent samples to be run on the 500-MHz wide bore spectrometer for the study “Microscopic Characterization of Porosity, Diffusivity, and Tortuosity in Single Particles of Hanford Sediments Using Nuclear Magnetic Resonance (NMR) Technique.”
- Gaetano Montelione and James Aramini, Rutgers University, Piscataway, New Jersey, sent samples to be run on the 750-MHz and 600-MHz spectrometers for the study “Structural Genomics of Eukaryotic Model Organisms.”
- Kristopher Ooms and Michelle Forgeron, University of Alberta, Edmonton, Alberta, Canada, used the 800-MHz and 750-MHz spectrometers for the studies “High-Field Solid-State ^{99}Ru NMR Spectroscopy in Inorganic and Organometallic Ruthenium Compounds” and “An Extended Study of Solid Molybdenum and Organometallic Magnesium Compounds Using ^{95}Mo and ^{25}Mg Nuclear Magnetic Resonance Spectroscopy.”
- Louis Pete Silks, Los Alamos National Laboratory, Los Alamos, New Mexico, sent samples to be run on the 500-MHz spectrometer for the study “Ultra-High Field NMR Studies of Stable Isotope Applications.”
- Michael Smerdon, Washington State University, Pullman, Washington, sent samples to be run on the 600-MHz spectrometer for the study “Structural Biology of Mammalian Chromatin High Mobility Group Protein HMGA1 and UV-Damaged DNA.”
- Suzanna K. Straus, University of British Columbia, Vancouver, British Columbia, Canada, used the 800-MHz spectrometer for the study “Development of Resolution Enhancement Techniques for the Complete Structure Determination of Fully $^{13}\text{C}/^{15}\text{N}$ -Labelled Peptides and Proteins Using Solid-State NMR.”

- Gabriele Varani and Thomas Leeper, University of Washington, Seattle, Washington, used the 800-MHz spectrometer for the study “Structure of Telomerase RNA,”
- Susan Wallace, University of Vermont, Burlington, Vermont, sent samples to be run on the 500-MHz and 600-MHz spectrometers for the study “Structural Studies of *Escherichia coli* Formamidopyrimidine DNA N-glycosylase and its Main Biological Substrate 8-oxoguanine.” Wallace, in collaboration with Michael Kennedy and Garry Buchko, Pacific Northwest National Laboratory, Richland, Washington, also sent samples to be run on the 500-MHz spectrometer for the study “Interaction of *Escherichia coli* Formamidopyrimidine-DNA Glycosylase (Fpg) With Damaged DNA Containing an 7,8-Dihydro-8-oxoguanine Lesion.”
- Brian D. Wood, Oregon State University, Corvallis, Oregon, used the 500-MHz wide bore spectrometer for the study “Continuing Exploration of NMR Imaging of Microorganisms in Porous Media Using NMR Microscopy.”

High-Performance Mass Spectrometry Facility

- Michael Daly, Uniformed Services University of Health Sciences, Bethesda, Maryland, used EMSL resources to perform data analysis on the “Comparative Display of *D. radiodurans* after exposure to Ionizing Radiation.” He is focusing on improving quantitation of $^{14}\text{N}/^{15}\text{N}$.
- Jim Fredrickson, Pacific Northwest National Laboratory, Richland, Washington, performed sample analyses on *Shewanella oneidensis* ranging from the comparison of cells grown under aerobic and anaerobic conditions to the comparison of protein expression profiles from wild type and mutant cells. Most of these samples were analyzed on the FTICR utilizing a range of techniques available in the laboratory including stable isotope labeling, membrane and cytosolic preparations, vesicle preparations and global tryptic lysate preparation.
- Michael Gerald Katze, University of Washington, Seattle, Washington, provided samples that are being analyzed at EMSL to study “Cellular Response to Hepatitis C Virus Infection: Global Quantitative Proteome AMT Tag Measurements of Cellular Protein Expression.”
- Mary Lipton, Pacific Northwest National Laboratory, Richland, Washington, and Sandra McCutchen-Maloney, Lawrence Livermore National Laboratory, Livermore, California, analyzed *Yersinia pestis* cells grown in ^{14}N media and isotopically depleted (^{15}N) media.
- Anil J Patwardhan, University of California-San Francisco, San Francisco, California, was provided data results from the strong cation exchange fractionation of the breast cancer cell membranes for his study of the “Identification and relative expression of membrane proteins in breast cancer cell lines.” He has provided additional samples for fractionation, labeling, and analysis.
- Wenzhong Xiao, Stanford University, Stanford, California, provided samples for “Functional Genomics and Proteomics of Mitochondria” studies. Staff collected relative abundance data for mitochondria in yeast, which were forwarded to the users.

Interfacial & Nanoscale Science Facility

- Jiji Antony, University of Idaho, Moscow, Idaho, used EMSL's scanning probe microscopes to obtain size and morphological information on iron nanoparticles she synthesized.
- Robert Fisher and Barbara Reine, Lab/Cor. Inc., Seattle, Washington, visited EMSL to study the cause of the deterioration in humid climates of cement roofing shingles containing cellulose fiber. One proposed mechanism is expansion and contraction of the mucilaginous sheath of the cyanobacteria *Scytonema* sp. filaments that have penetrated the shingles. Cyanobacteria-infected shingles were repeatedly hydrated and dehydrated using the ElectroScan Environmental Scanning Electron Microscope. The observations were videotaped, and the tapes are being analyzed to see if swelling occurred.
- Kelli Griffin, University of Washington, Seattle, Washington, studied sputter-deposited TiO₂ films on LaAlO₃ and silicon using high-resolution X-ray diffraction, grazing-incidence X-ray diffraction, X-ray reflectivity, Rutherford backscattering spectroscopy, and atomic force microscopy. Results showed that films grown on LaAlO₃ were epitaxial and adopted the structure of anatase <001>. By contrast, the co-deposited films on silicon were polycrystalline mixtures of anatase and rutile.
- Steven Limmer, University of Washington, Seattle, Washington, used high-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray microanalysis to characterize V₂O₅ single crystal nanorods grown at the University of Washington. Steven determined the growth direction and, based on these results, will be able to selectively modify the nanorod chemistry and the morphology. Some nanorods showed a core-shell structure.
- Kunakorn Poochinda, University of Washington, Seattle, Washington, used the Auger electron spectrometer to obtain compositional information on gallium nitride films as a function of depth. He is growing the GaN thin films by MOCVD to investigate the possibility of producing novel light detection devices.
- Brad Roberts, University of Washington, Seattle, Washington, studied sputter-deposited chromium- and cobalt-doped ZnO films grown on silicon using grazing-incidence X-ray diffraction, X-ray reflectivity, Rutherford backscattering spectroscopy, and atomic force microscopy. Results showed that the films were mixtures of hexagonal and cubic ZnO-type polymorphs.
- Harry J. Whitlow, Lund Institute of Technology, Lund, Sweden, gave the seminar "Nanometre Scale Proton Beam Lithography: Breaking the Proximity Exposure Barrier?"
- Nirbhay Yadav, University of Western Sydney, Sydney, Australia, visited the accelerator facility to work on his Masters dissertation. During his one and a half month stay in Richland, Nirbhay was trained as qualified operator of the accelerator at EMSL. He also conducted experiments in quantification of trace arsenic concentration in activated carbon samples using proton induced X-ray emission (PIXE).

Molecular Science Computing Facility

- Bob Carling, Deputy Director from the Sandia Combustion Research Facility, Livermore, California, visited EMSL on October 3, 2003. He headed a small delegation hosted by Bill Rogers and Allison Campbell.
- Gerardo Cisneros-Stoianowsk, SGI, presented a two-and-a-half-day training session on techniques for application development and optimization for the Silicon Graphics, Inc., Altix 3000 machine recently acquired by PNNL. This is a 128-processor shared memory machine based on the Itanium 64 chip. The session was attended by 10 to 12 users/potential users of the machine and included some one-on-one discussions. Topics covered included compiling, machine architecture, memory management strategies, development tools, application interfaces, and performance tuning.
- Kristin Hermann (Figure 22), University of Arizona, Tuscon, Arizona, used Ecce and NWChem to investigate the fixed charge derivative tris-(2,4,6-trimethoxyphenyl) phosphonium ion bonded to short peptide sequences. Using the three-panel monitor in the Graphics & Visualization Lab, she studied in three dimensions the molecules she has been fragmenting in the mass spectrometer. The new HP supercomputer enabled this work to be performed in a much shorter time period.
- Masayuki Inui and Seiichi Matsuo, Research Institute of Innovative Technology for the Earth, Kyoto, Japan, visited EMSL to learn more about the research conducted at PNNL and discuss the possibility of building a collaboration in the area of bacterial proteomics.
- The members of the EMSL Science Advisory Committee toured the MSCF on October 17, 2003.



Figure 22. Kristin Hermann working in the MSCF Graphics & Visualization Lab in EMSL.

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

- Academy of Sciences of the Czech Republic, Prague, Czech Republic
- Albert Einstein College of Medicine, Bronx, New York
- Argonne National Laboratory, Argonne, Illinois
- California State University, Fullerton, California
- Central China Normal University, Wuhan, China
- China University of Geosciences, Wuhan, China
- Computer Science Corp., Wright-Patterson AFB, Virginia
- Curtin University of Technology, Perth, Australia
- Georgetown University, Washington, D.C.
- Griffith University, Brisbane, Australia

- Hitachi Europe GmbH, Feldkirchen, Germany
- Hospital for Sick Children, Toronto, Ontario, Canada
- Institute of Biotechnology, Helsinki, Finland
- Institute of Solid State Physics, Riga, Latvia
- Kinetana Group Inc., Alberta, Canada
- Korea National University of Education, Chungbuk, South Korea
- Lundbeck, Valby, Denmark
- Nanjing Normal University, Nanjing, China
- National Cancer Institute, Frederick, Maryland
- National Chiao Tung University, Hsinchn City, Taiwan
- NEC High Performance, Prinzenallee, Germany
- Oak Ridge National Laboratory, Oak Ridge, Tennessee
- Ohio State University, Columbus, Ohio
- Pace University, New York City, New York
- Pfizer, Chesterfield, Montana
- Rutgers University, Piscataway, New Jersey
- Savannah River Site, Aiken, South Carolina
- St. Petersburg State University, St. Petersburg, Russia
- Targacept Inc., Winston Salem, North Carolina
- Technical University Kaiserslauter, Kaiserslauter, Germany
- Tel Aviv University, Tel Aviv, Israel
- Universidad de Castilla-La Manch, Ciudad Real, Spain
- Universidad del Pais Vasco, Bilbao, Spain
- Universidad Nacional de San Luis, San Luis, Argentina
- Universidade Federal de Pernambuco, Recife, Brazil
- Universidade Federal de Uberland, Federal, Uberlandia, Brazil
- Universita' di Cagliari, Monserrato, Italy
- Universite Louis Pasteur, Illkirch, France
- University of Akron, Akron, Ohio
- University of Bielefeld, Bielefeld, Germany
- University of California, Davis, California
- University of Coimbra - Faculty of Sciences and Technology, Coimbra, Portugal
- University of Heidelberg, Heidelberg, Germany
- University of Illinois, Champaign, Illinois
- University of Missouri, Kansas City, Missouri
- University of New Mexico, Albuquerque, New Mexico
- University of Rhode Island, Kingston, Rhode Island
- University of Science and Technology of China, Hefei, China
- University of Washington, Seattle, Washington
- University of Zaragoza, Zaragoza, Spain
- Washington State University, Pullman, Washington
- Washington State University, Tri-Cities, Washington

- Wayne State University, Detroit, Michigan
- Wilkes University, Wilkes-Barre, Pennsylvania

New EMSL Staff

Marat Valiev was hired as a Senior Research Scientist II in September. He will be involved with computational chemistry and biochemistry research in the Molecular Sciences Software group, primarily working on the development and implementation of Quantum Mechanical and Molecular Mechanical (QM/MM) methodologies in NWChem, the computational chemistry software suite for massively parallel computers developed at PNNL. Prior to joining EMSL, Marat was a staff member in the University of California, San Diego's Chemistry and Biochemistry department.

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