William R. Wiley EMSL
Environmental Molecular Sciences Laboratory

Office of Science
U.S. DEPARTMENT OF ENERGY

Highlights from Computational Research at EMSL

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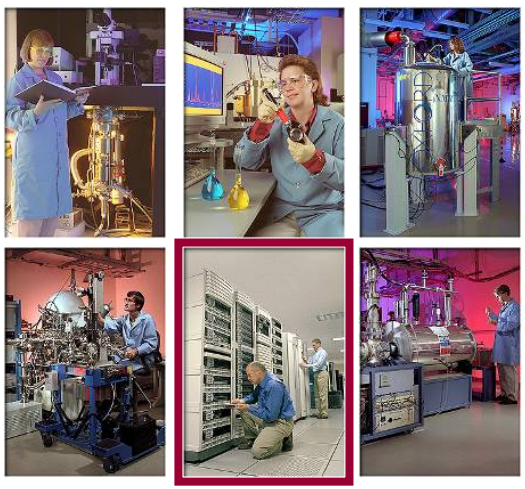
Molecular Science Computing Facility

- **Leading Department of Energy user facility for computational chemistry, biochemistry and environmental problems, integrating computation with theory and experiment.**
- **Facility focuses on providing the right hardware, software and consulting to teams of computational scientists toward understanding grand challenge scientific problems.**

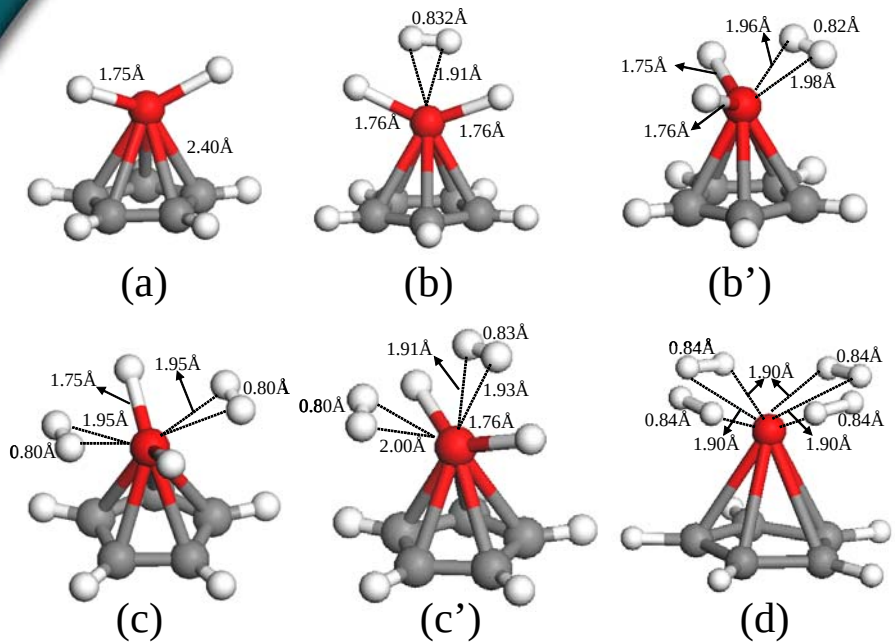


Integrated with the experimental facilities in EMSL

- Computational Grand-Challenge Projects
- EMSL Science Theme Projects
- EMSL Grand Challenge Projects
- Office of Science INCITE Projects
- General or Pilot Projects
- Capability Development

H-storage and the 18-electron Rule

Virginia Commonwealth University



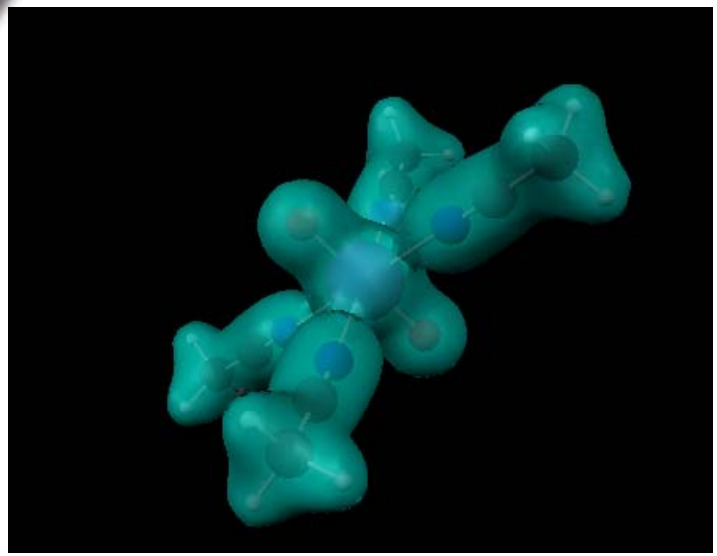
Optimized structures of $TiC_5H_5(H_2)_n$ where n=1-4. Energy difference between (b) and (b') is 0.12 eV, between (c) and (c') is 0.02 eV with (b) and (c) being lower in energy than (b') and (c').

- Transition metal complexes are a possibility for H-storage are where H_2 molecules are ligands.
- Here Ti attached to C_5H_5 binds up to four H_2 molecules per Ti atom, 9 wt % hydrogen.
- Kinetics are fast and the binding energy is small enough (0.55 eV/H_2) to desorb near 100 ˚C.
- We have analyzed the maximum number of H_2 molecules that can be adsorbed and the nature of their bonding.
- Charge transfer from the H_2 bonding orbital to the empty d_{xy} and d_{x2-y2} orbitals of Ti is primarily responsible for hydrogen binding
- The 18-electron rule can be used to design new organometallic systems for H-storage; early transition metals being better suited for optimal adsorption/desorption of hydrogen.

B. Kiran, A. K. Kandalam, P. Jena, "Hydrogen Storage and the 18-electron Rule", *J. Chem. Phys.* 124, 224703 (2006).

Computational Studies in Actinide Chemistry

Free University of Amsterdam



Electron density distribution in a uranyl cation with four acetonitrile molecules.

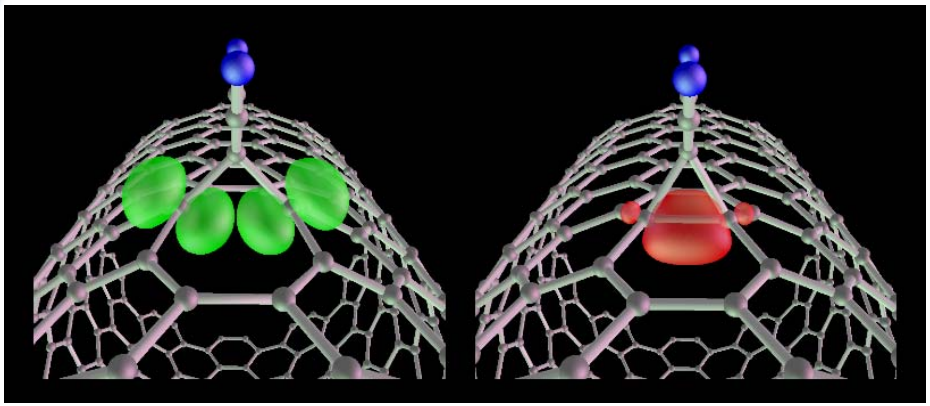
- Benchmark all-electron fully relativistic MR-CCSD calculations with the DIRAC program on the small actinide complexes
- ADF calculations to interpret infrared multi-photon dissociation experiments of uranyl complexes
- MPP2 is well-suited for these computationally demanding calculations

G. S. Groenewold, A. K. Gianotto, K. C. Cossel, M. J. Van Stipdonk, D. T. Moore, N. Polfer, J. Oomens, W. A. de Jong, L. Visscher, "Vibrational Spectroscopy of Mass-Selected [UO2(ligand)n]2+ Complexes in the Gas Phase: Comparison with Theory" *J. Am. Chem. Soc.* 128, 4802 (2006)

Cycloaddition Functionalizations Preserve or Control Carbon Nanotube Conductance

MIT/MSE

Two tautomeric states show different conductance states suggesting a novel conductance-control mechanism

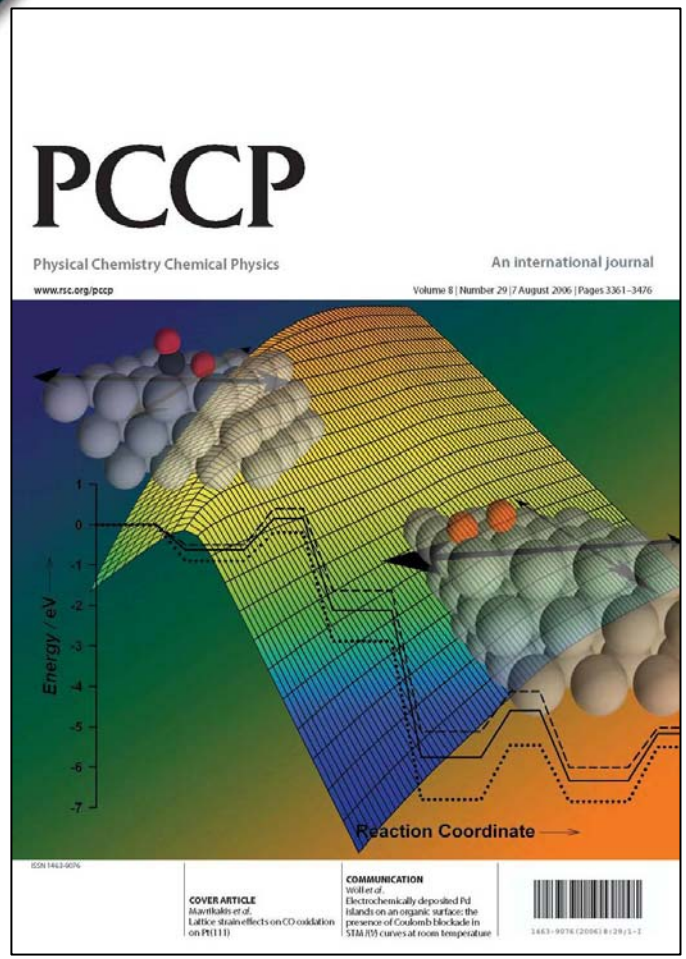


Orbital rehybridization through bond breaking and forming can be equally applied to both semiconducting and metallic nanotubes.

- An extensive theoretical study on the energetics and quantum conductance of armchair carbon nanotubes functionalized with carbenes or nitrenes was performed.
- The groups are attached to neighboring carbon atoms forming a three-membered ring.
- The diameter of the tubes, relative angle of the sidewall carbon-carbon bond, and the chemical nature of the groups, determine the stability of the bond between the two sidewall carbons.

Y.-S. Lee and N. Marzari, "Cycloaddition functionalizations to preserve or control the conductance of carbon nanotubes", Phys. Rev. Lett. 97, 116801 (2006).

Chemo-mechanical coupling: Lattice strain effects on CO+O/Pt(111)



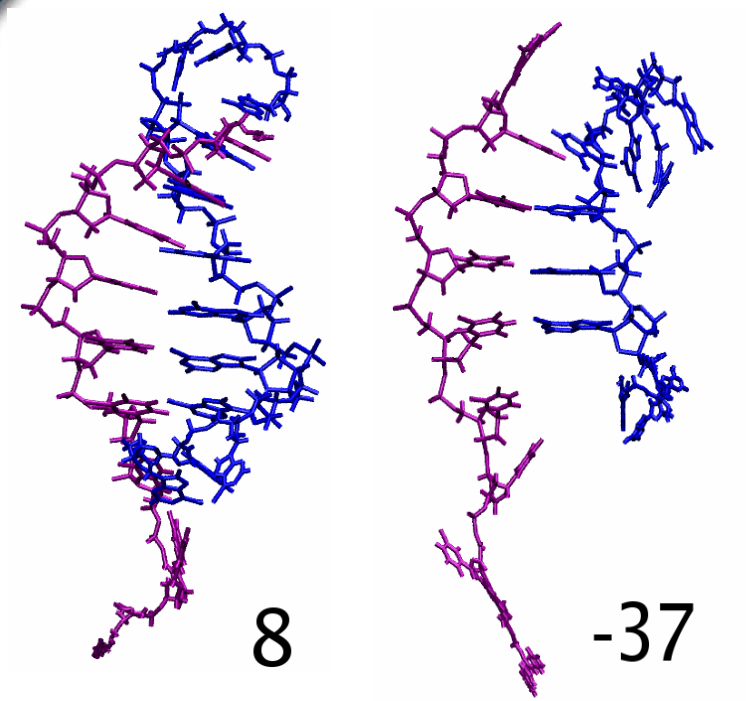
- We calculated the effect of surface strain on the catalytic activity of Pt using density functional theory (DFT).
- Cirak *et al.*[1] observed oscillatory behavior of an ultra-thin Pt(110) single crystal during CO oxidation and studied the coupling between chemical, thermodynamic, and mechanical phenomena during this process.
- By coupling DFT results with a microkinetic model, we could not only demonstrate the significant effect of strain on the catalytic activity of Pt(111), but we could also show that the rate limiting step can be changed by manipulating strain.

[1] F. Cirak, J. E. Cisternas, A. M. Cuitino, G. Ertl, P. Holmes, I. G. Kevrekidis, M. Oritz, H. H. Rotermund, M. Schunack, J. Wolff, *Science*, **300**, 1932 (2003)

L. Grabow, Y. Xu, M. Mavrikakis, "Lattice strain effects on CO oxidation on Pt(111)" *Physical Chemistry Chemical Physics*, 8, 3369 (2006), including Cover Page Image.

Multiscale Modeling of Biochip Systems

University of Houston



Conformations of DNA at two different values of the first principal component while all other principal components are kept at zero.

- Molecular dynamics simulation of a 12 base-pair duplex DNA(dA)12.(dT)12 in 0.1M salt solution to model DNA melting.
- The temperature was set to 401 °K.
- To understand how the DNA duplex melts, we applied Principal Component Analysis (PCA) to analyze the trajectory between 79 and 86.2 ns.
- Coordinates of all atoms are used to construct the covariance matrix.
- The first principal component is nearly constant between 79 and 83 ns, but then starts to decrease
- The first principal component is -83 at 86 ns.
- All other principal components are kept at zero.
- As the first principal component decreases, both the A- and T-strands untwist and the basepairs near the ends start to separate.

Capture of Uranyl by the Lipopolysaccharide Membrane of *Pseudomonas aeruginosa.*

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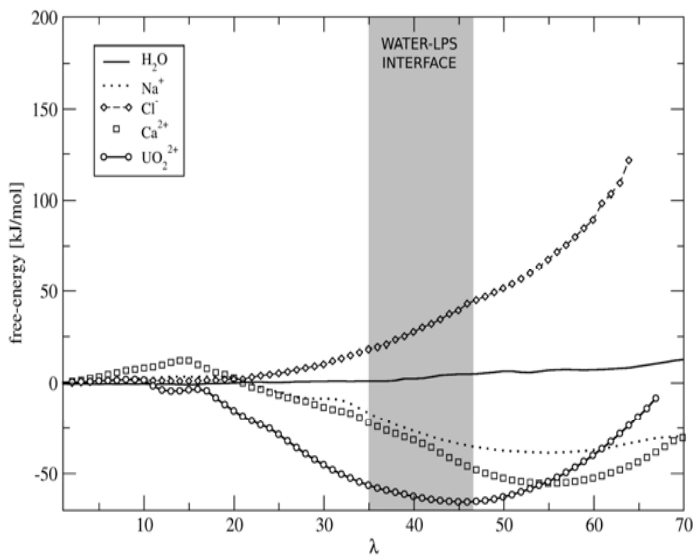


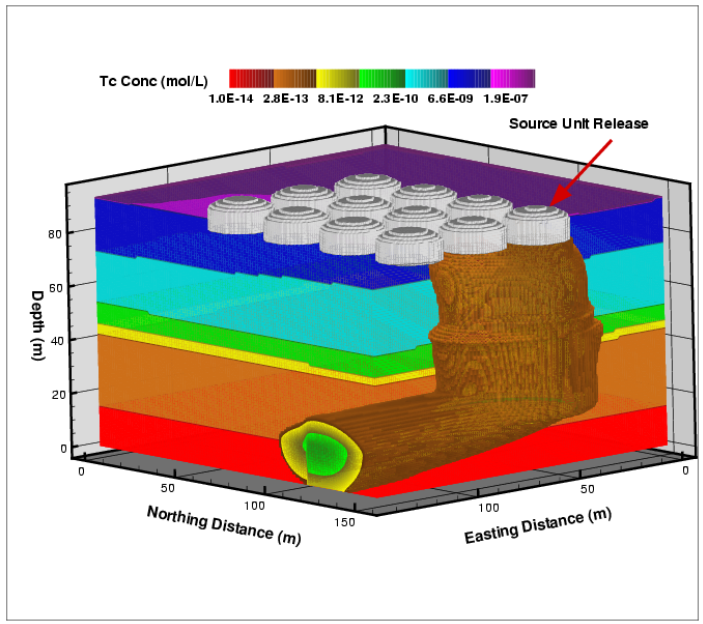
- Free-energy profile for the potential-of-mean force molecular dynamics as a function of λ.
- The water-LPS interface is shown as a grey area.
- Inset shows specific interactions between the ions and carboxyl groups of the microbial membrane.

- Heavy metal contaminants cannot be destroyed, only concentrated and contained for recycling or final disposal.
- Microorganisms able to uptake, reduce and deposit metal contaminants through their cell wall have potential use in bioremediation.
- A gram-negative microbe's outer membrane can be highly non-symmetric with an electrostatic potential gradient
- Effective cleanup requires a cell wall capable of absorbing the desired contaminant.
- Characterization of actinide complexes in solution, predicting transport in the environment, and their uptake process by microbial outer membranes is imperative for success.

R. D. Lins, E. R. Vorpagel, M. Guglielmi and T. P. Straatsma, "Characterization of Uranyl Uptake by the Rough Lipopolysaccharide Membrane of *Pseudomonas aeruginosa*" Submitted to *Geochimica et Cosmochimica Acta*, (2007).

Long Term Fate & Transport Modeling

PNNL



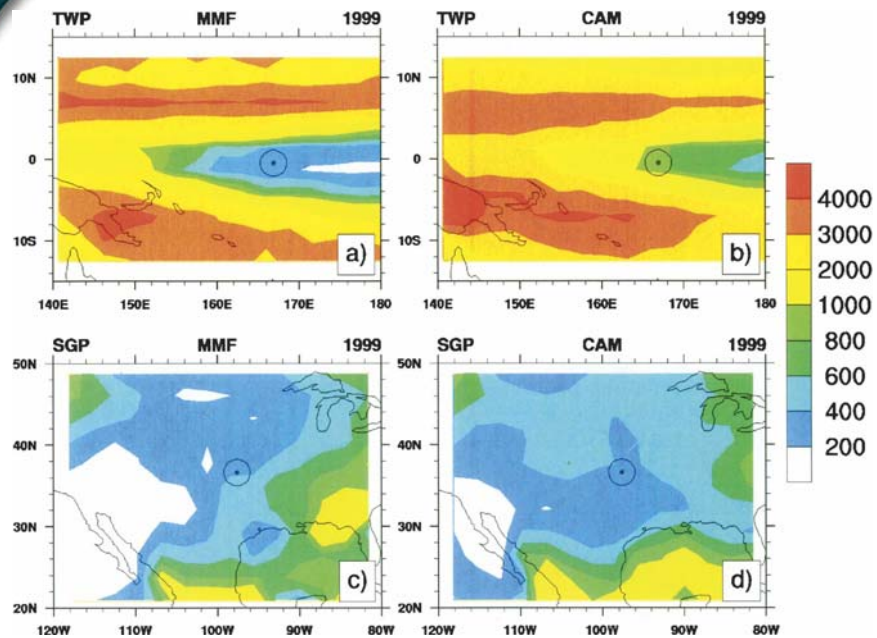
Subsurface ^{99}Tc concentration distribution after 1000 years of simulation at the Hanford S Farm

- Caustic radioactive wastes that leak induce mineral dissolution and subsequent precipitation.
- Effects of secondary mineral precipitates on flow path and radionuclide immobilization were investigated experimentally.
- Variably saturated flow and multi-solute reactive transport simulations were performed to investigate different potential contaminant source scenarios that could pose long-term risks to groundwater from the closure of the Hanford Tank Farms.

W. Um, R. J. Serne, S. B. Yabusaki, A. T. Owen, "Enhanced radionuclide immobilization and flow path modifications by dissolution and secondary precipitates" *J. Environ. Quality* 34, 1404 (2005)

Superparameterization: A New Paradigm for Climate Modeling

PNNL



Annual precipitation amount (mm) as predicted by the (a), (c) MMF and (b), (d) CAM for the (a), (b) tropical western Pacific and (c), (d) SGP regions for 1999. Locations of the two ARM sites are encircled. The observed precipitation amounts are 358 and 1031 mm for the TWP and SGP sites, respectively.

- Parallel simulations were carried out using superparameterization within the Multi-scale Modeling Framework (MMF) and the Community Atmospheric Model (CAM)
- Comparison of the predicted annual precipitation with surface observations indicate that the MMF provides a much better simulation of the dryer equatorial tongue.
- Observed rainfall at Nauru is 358 mm, in excellent agreement with the MMF results.
- The two model simulations are very similar in continental mid-latitudes, both predict rainfall rates that are less than one half of the amount observed at the Southern Great Plains (SGP) site.

M. Ovtchinnikov, T. Ackerman, R. Marchand, "Evaluation of the Multiscale Modeling Framework Using Data from the Atmospheric Radiation Measurement Program" *J. Climate,* 19, 1716 (2006)

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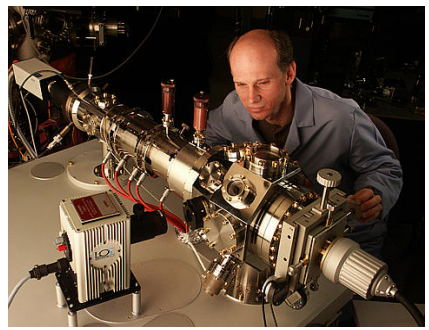

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