Proposal ID number:
GC34900

Title of the proposal:
Computational Chemical Dynamics of Complex Systems

Primary author name and institution:
Donald G. Truhlar, University of Minnesota

Collaborative project between the University of Minnesota, University of South Carolina, and the Environmental Molecular Sciences Laboratory (EMSL)

Summary of the results achieved since the last progress report

Period covered: October 1, 2010 – June 1, 2011 (second year)
Date of report: June 1, 2011

The goal of this ongoing project is to apply powerful new simulation techniques to tackle computationally challenging problems in chemical dynamics, with special emphasis on the critical problems in environmental science and chemical engineering facing the U. S. Department of Energy (DOE) and the nation. Our studies involve electrochemistry, heterogeneous catalysis, nanoparticles, solid-state dynamics, and photochemistry. Our computations are carried out with new high-throughput integrated software that we are developing. Our up-to-date accomplishments and activities in the fiscal year of 2010–11 are overviewed below.

Validation of electronic structure methods for studying the intermolecular interactions in various systems (J. Alecu, B. Averkiev, L. Fiedler, H. Leverentz, S. Luo, A. Marenich, S. L. Mielke, E. Papajak, O. Tishchenko, B. Wang, T. Yu, J. Zhen, and D. G. Truhlar [PI], University of Minnesota)

Thanks to the EMSL, we have been making progress on the development and testing of a number of new methods for the use of high-end computing to various chemical and biochemical applications including catalysis. A substantial portion of the allocated computational time so far has been used towards the development of new improved density functional theory (DFT) methods. These computations involve benchmark calculations of organometallic compounds and metal clusters by using coupled cluster calculations with single and double excitations and quasiperturbative treatment of connected triple excitations, coupled cluster based on Brueckner orbitals with double excitations and a quasiperturbative treatment of connected triple excitations, and the powerful explicitly-correlated method CCSD(T)-F12. In particular, we have been using the EMSL supercomputer to obtain the benchmark data on several dozen isomerization reactions that involve a number of large organic molecules containing up to 81 atoms. We also explore the use of diffuse basis functions for electronic structure calculations by DFT and wave function theory to calculate dynamics of complex reactions in a cost efficient manner. In the past year, we have also initiated a study of the intermolecular interactions between several atmospheric species (e.g., $N_2...N_2$, $O_2...O_2$, $N_2...O_2$) under our Air Force Office of Scientific Research project.

Large-scale calculations on combustion mechanisms of biofuels (J. Alecu, B. Averkiev, L. Fiedler, H. Leverentz, S. Luo, A. Marenich, S. L. Mielke, E. Papajak, O. Tishchenko, B. Wang, T. Yu, J. Zhen, and D. G. Truhlar [PI], University of Minnesota)

We continue our large-scale calculations on combustion mechanisms of biofuels. This project includes a study of the mechanism of several chemical reactions involving $n$-butanol which has been recently proposed as an alternative renewable fuel to conventional gasoline and diesel fuels. It is essential that the mechanism for the combustion of $n$-butanol be thoroughly explored and understood in order to efficiently implement this resource in commercial vehicles. The success of this project is a key element in the DOE plans to improve the country’s energy efficiency and self-sufficiency. This work is being carried out as part of the Combustion Energy Frontier Research Center, and it is funded by two grants from the DOE. A critical part of our computations under this project has been performed at the EMSL computational facility.

Reactivity and dynamics of nanoparticles, amorphous solids, and clusters (S. Ammal, S. Suthirakun, and A. Heyden [co-PI], University of South Carolina)

We continue our work on the development of scalable multiscale algorithms for the rational design of new electrode materials for solid oxide fuel cells (SOFCs). In particular, we have been investigating the effects of $n$- and $p$-type B-site dopants on the electronic and ionic conductivity of SrTiO$_3$ perovskite structures by studying the Nb- and Ga-doped SrTiO$_3$ systems under various dopant concentrations. We have evaluated the thermodynamic stability of doped SrTiO$_3$ at synthesized and anodic SOFC conditions and we have found that 20% Nb-doped Sr-deficient SrTiO$_3$ ($Sr_{0.9}Ti_{0.8}Nb_{0.2}O_3$) transforms to non-Sr-deficient phase in reducing environments at high temperature, which leads to an increased number of available charge carriers and improvement in electronic conductivity. Moreover, both oxygen deficiency and oxygen-ion conductivity can be increased by doping with Ga. Doping 20% Nb-doped SrTiO$_3$ with 10% Ga enhances ionic conductivity without diminishing the number of charge carriers and electronic conductivity. As a result, mixed ionic/electronic conductivity can be achieved. However, 20% Ga doping decreases the electronic conductivity of the material without increasing ionic conductivity. We also continue to investigate the catalytic activity and selectivity of the three-phase boundary of Pt supported TiO$_2$ and CeO$_2$ catalysts for the water-gas shift (WGS) reaction. The initial objective of this project has been to better understand the oxidation state of...
interface metal atoms and the role of interfacial oxygen atoms. Our calculations reveal that the formation of oxygen vacancies at both interfaces is thermodynamically favorable under WGS reaction conditions while the adsorption of oxygen atoms on surface Pt atoms is unfavorable. CO adsors strongly on the surface Pt atoms in both cases and only interfacial Pt atoms are expected to be available for catalysis. Surprisingly, the presence of adsorbed CO on surface Pt atoms seems to promote the adsorption of hydrogen atoms at the interface for CeO$_2$ supports, however, it has a negative effect for TiO$_2$ supports. The information obtained from this analysis is currently being used to better understand the reaction mechanism and rate limiting reaction steps of the WGS at the interface catalysts of Pt$_x$/TiO$_2$ and Pt$_x$/CeO$_2$.

**Molecular dynamics simulation of protein kinase (A. Cembran and J. Gao [co-PI], University of Minnesota)**

Protein kinase A (PKA) is involved in numerous cellular signaling events and its activity is subject to both space and time regulation. N-myristoylation of the N-terminal of PKA-C subunit is one of such regulatory mechanisms. Thermodynamics, kinetics and spectroscopic experiments suggest that phosphorylation at Ser10 can further tune the effects of myristoylation by acting as a switch that shifts the equilibrium between the myristoyl group inside and outside the protein’s hydrophobic pocket. In order to investigate in detail the structure and dynamics of myristoylated PKA-C, and to probe the effects of Ser10 phosphorylation, we have employed all-atoms molecular dynamics simulations on the myristoylated PKA-C in explicit solvent. Next, we will investigate the differences between the phosphorylated and unphosphorylated isoforms in a more quantitative way through replica-exchange molecular dynamics simulation and through the adaptive biasing force method. Specific interactions of the myristoylated PKA-C with the explicit lipid bilayer will also be investigated.

**Computational studies of complex chemical transformations: An application to the hyponitrite radical and the nitrosyl hyponitrite anion in aqueous solution (S. Lymar and M. Valiev [co-PI], EMSL)**

Experimental UV absorption spectroscopy is a powerful technique to probe the structure of reacting solute species in liquid phase, but the interpretation could be uncertain if the absorption signature of individual solute molecules is not known a priori. Theoretical modeling has the capacity to fill this gap provided that both electronic structure effects and the solvent environment are described properly. This is the area of research that we have been pursuing with the experimental group of Sergei Lymar (Brookhaven National Laboratory), which involves mechanistic analysis of UV spectra of solvated NO-based radical species. In this project, we have been studying the N$_2$O$_2^–$ and N$_3$O$_5^–$ species in aqueous solution. These systems are important intermediates in biological and environmental reductive chemistries of NO. Based on correlation between the experimental and computed UV spectra, we have found that the N$_2$O$_2^–$ radical exists predominantly in the trans-form, and the aqueous N$_3$O$_5^–$ anion exists in both the cis-symmetric and linear trans-asymmetric forms. It was also found that some of the previous assignments in the experimental spectra involving these species should be revisited.

**List of publications**


**Description of work to be performed over the coming year**

We would like to request an extension of our CIR project to the third year. As of May 16 (2011), we have used ~600,000 node-hours or 75% of our FY10 allocation (800,000 node-hours). Based on our current usage rate and current annual allocation, we would like to request 1,200,000 node-hours for the next year. During the next period, we will complete each of the five subprojects described above. In addition, we plan to work on the following topic:

**Multi-scale simulations of self-aggregating cyanine dyes in complex environments – combined RISM and QM/MM approach (G. N. Chuev and M. Valiev, EMSL)**

Cyanine dyes form various nanostructures with semiconductors and metal nanoparticles. A large variety of meso- and macrostructures of dye aggregates has been observed, depending on experimental conditions. These structures can be characterized by red or blue shifts of their absorption spectra with respect to those of monomers. In general, the difference in the spectra is attributed to the stacking order of monomers in these assemblies. However, definitive supramolecular structures of the aggregates have never been determined directly and the detailed structural mechanisms of the cyanine dyes self-aggregation in solution still remain the subject of much speculation. This study will involve a fully atomistic modeling of the aggregates with an accurate treatment of solvent effects by the integral equation theory of molecular liquids. Such an approach allows for reducing the computational costs of treating the solvent effects by a factor of ~100 in comparison with molecular dynamics or Monte-Carlo simulations. We believe that the reference interaction site model (RISM) combined with the quantum mechanics/molecular mechanics (QM/MM) approach implemented in NWChem may provide key answers to many fundamental questions in regard to these interesting systems. In addition, we propose to extend NWChem’s QM/MM+RISM interface to the treatment of absorption spectra with the use of high-level ab initio methods such as coupled cluster theory. The resulting methodology will then be tested against self-aggregating cyanine dyes complexes involving hundreds of monomers.