Computational Chemical Dynamics: From Gas–Phase to Condensed–Phase Systems

Poster Presentations

October 7, 2004

6:30–10:00 p.m.

Great Hall
Coffman Memorial Union
University of Minnesota
Minneapolis, Minnesota
Table of Contents

Location and Schedule 1
Poster Abstracts 2
Index of Authors 41
Location and Schedule

The pizza/poster session is from 6:30 to 10:00 p.m. in the Great Hall (ground floor) of Coffman Memorial Union on Thursday, October 7. The schedule for the poster session is as follows:

- 6:30 to 7:15 p.m. Pizza, other refreshments, and poster setup*
- 7:15 to 8:05 p.m. Poster session A
- 8:05 to 8:55 p.m. Poster session B
- 8:55 to 9:45 p.m. Poster session C
- 9:45 to 10:00 p.m. Poster take down

*Poster boards and pins will be furnished.
Poster Abstracts

Poster A1

Amos Anderson, Daniel Fisher, Albert Cervantes, Mario Blanco, Peter Schroder, and William A. Goddard III
California Institute of Technology

Quantum Monte Carlo Quantum Mechanics on Game Boards

Quantum Monte Carlo (QMC) methods integrate the Schrödinger equation by Monte Carlo integration techniques, allowing one to obtain arbitrary accurate results. The problem is that QMC calculations demand enormous computing resources, so that it has not been practical to use these methods for the many important problems in catalysis, pharma, and materials sciences that need much more accurate results. On the other hand QMC is extremely parallelizable, with minimal memory and communication requirements.

Driven by the multi-billion dollar computer gaming market, the computational power of graphical processing units (GPUs) now exceed CPUs in terms of performance and price. Thus current GPUs are capable of ~ 50 billion floating point operations per second (GFLOPS) peak performance, comparable to the ~ 7 GFLOPS of a Pentium 4. In addition, the performance of GPUs doubles every 6 months compared to the 18 month doubling time of Moore’s Law, indicating that the performance gap will increase exponentially. These GPUs have become high-language programmable under the single-instruction multiple-data (SIMD) streaming paradigm, making it reasonable to consider using GPUs to construct a very cheap supercomputer for scientific computations. The major impediment is that the aspects of the architecture of GPUs that allows the great performance also restricts the programmability. Thus GPUs have limits to the length of the program, the memory available, and the precision of computations.

We have reformulated the QMC algorithms to make calculations feasible on GPUs and are implementing these on GPUs. We plan to build a QMC/GPU supercomputer composed of ~ 200 GPU/ 100 CPU units that we estimate may provide 10 Tera Flop peak performance at a cost of less than $200K.

Poster A2

Sudeep Bhattacharyay, Marian T. Stankovich, and Jiali Gao
University of Minnesota

A QM/MM Simulation of the Catalytic Proton and Hydride Transfer Reactions of Medium Chain Acyl-Coa Dehydrogenase: Modeling the Role of Active Site Mutants on Energetics, Substrate Binding and Catalytic Mechanism

Medium chain acyl-CoA dehydrogenase (MCAD) catalyzes the α,β-dehydrogenation of fatty acid acyl-CoAs. The reaction is a two-step process—a proton abstraction, followed by a hydride transfer step. Using a hybrid QM/MM simulation we have calculated the potential of mean forces for the catalytic reactions in wild type enzyme and two of its mutant forms. Energy profiles obtained for the two reaction steps indicate that they follow a stepwise mechanism rather than concerted.

Analyses of structural changes along the reaction path of wild type enzyme reveal a large hydrogen-bonding network encompassing the reaction center—the thioester carbonyl group. Furthermore, it shows an arginine residue (R256), absolutely conserved in the substrate-binding domain of this group of enzyme, to be at the center of this network and contribute to the stabilization of both the transition states. Computations starting from two different conformations of this residue results two alternate active site states, only one of which corresponds to the active enzyme.
Simulation of the disease-causing T168A mutant of this enzyme shows loss of one of its flavin ring H-bonding interactions. However, this mutation does not have a significant impact into the energetics of the reaction steps. The computed overall reaction barriers for this mutant remains unchanged, agreeable to the experimental results.

We also conducted a model mutation of R256 (mentioned before) residue to glutamine. Analysis of the active site structures, obtained from molecular dynamics trajectory of the R256Q-MCAD mutant enzyme, shows that the reaction center of the substrate has completely lost its relative orientation in the active site when compared to the wild type and T168A mutant. Free energy profiles also demonstrate that activation barriers for both the catalytic steps have been increased due to this single mutation. However, the impact of this mutation is more pronounced for the hydride transfer barrier which is increased by ~5 kcal/mol compared to the wild type. Two very important predictions come from these simulation results. First, we predict that the binding affinity of the substrate will be severely compromised in this case. Secondly, the mutant enzyme will have negligible catalytic activity compared to the wild type.

**Poster A3**

Arindam Chakraborty and Donald. G. Truhlar

*Calculation of the Quantum Mechanical Thermal Rate Constant for the OH + H₂ → H₂O + H Reaction Using Flux Autocorrelation Function*

The thermal rate constant of the three-dimensional OH + H₂ → H₂O + H reaction was computed using flux autocorrelation functions. We have used a time-independent L² basis set for a converged calculation for total angular momentum zero and the separable rotation approximation for higher total angular momentum. The basis functions used for the calculations were formed using a product of distributed Gaussian functions and harmonic oscillator functions. Two modes that actively participated in the bond-making process were treated using two-dimensional distributed Gaussian functions, and the remaining modes were treated using harmonic oscillator functions. The eigenvalues and eigenvectors of the Hamiltonian were obtained by solving the resulting generalized eigenvalue equation. The flux autocorrelation function was represented in the basis formed by the eigenvectors of the Hamiltonian and the rate constant was obtained by integrating the flux autocorrelation function for a variationally determined dividing surface. The choice of the final time to which the integration is carried is determined by identifying a plateau region. The potential energy surface is from Wu, Schatz, Lendvay, Fang, and Harding (WSLFH). The calculated thermal rate constant results were compared with values computed by wave packet methods.

**Poster A4**

S. A. Corcelli, C. P. Lawrence, J. R. Schmidt, and J. L. Skinner

University of Wisconsin,

*Computational Strategies for Ultrafast Vibrational Spectroscopy: Applications to Water and Aqueous Solutions*

We present a new approach that combines electronic structure (ES) methods and molecular dynamics (MD) simulations for investigating the vibrational spectroscopy of condensed phase systems. This approach was first applied to the OH stretch band of dilute HOD in liquid D₂O and the OD stretch band of dilute HOD in liquid H₂O. OH and OD anharmonic frequencies and their corresponding infrared and raman transition intensities were calculated using density functional methods for 100 HOD-(D₂O)ₙ and HOD-(H₂O)ₙ (ₙ = 4 – 9) clusters randomly selected from the liquid water simulations. It was found that the infrared transition dipole moments vary considerably with environment, while the raman intensities do not. The ES frequencies and transition dipole moments were both found to linearly correlate (r = 0.9) with the component of the electric field from the solvent along the bond of interest. These linear relationships were used in MD simulations to compute the frequency time-correlation function (FTCF) and the infrared and raman absorption line shapes. FTCFs were calculated for
three different water models: TIP4P, SPC/E, and SPC-FQ. The long time decay of the FTCF for the polarizable SPC-FQ model (1.45 ps) compared more favorably with recent vibrational echo experiments (1.4 ps) than the fixed charge models SPC/E (1.0 ps) and TIP4P (0.9 ps). The infrared and raman absorption line shapes for the SPC-FQ model were in qualitative agreement with experiment over the temperature range 10 °C – 90 °C. To demonstrate the transferability of the combined ES/MD approach, the vibrational spectroscopy of aqueous solutions of N-methylacetamide (NMA) and urea was investigated.

**Poster A5**

**Benjamin A. Ellingson** and Donald G. Truhlar  
University of Minnesota

**Computational Study and Dynamics Calculation of the Abstraction Reaction Between Hydroxyl Radical and Dimethyl Sulfide**

The primary organosulfur compound emitted into the atmosphere is dimethyl sulfide (DMS), which is released through biomass decay in oceans and the incomplete combustion of fossil fuels. The rate of the abstraction of hydrogen from DMS by a hydroxyl radical (DMS + OH• → DMS• + H₂O) is important for understanding the removal of OH radicals in the stratospheric ozone layer. We determined the rate constant using variational transition state theory with multidimensional tunneling contributions. Computational methods were first applied to the hydrogen sulfide plus hydroxyl radical system to determine which methods were most appropriate for sulfur containing systems. The potential energy surface was determined by selecting levels of theory that reproduce selected experimental results for this simpler reaction while minimizing computational cost. Hydrogen sulfide is also important in atmospheric chemistry and the rate constant for H₂S + OH• → HS• + H₂O has also been calculated.

This work was supported by the Department of Energy, Office of Basic Sciences.

**Poster A6**

**Alfred D. French**  
U. S. Department of Agriculture

**Prediction of Crystalline Carbohydrate Conformations With Gas Phase QM Energy Minimization Studies of Non-Hydroxylated Analogs**

When calculating energy surfaces for disaccharides based on varied interglycosidic linkage torsion angles, stereoelectronic effects in carbohydrates can best be calculated by electronic structure theory. However, because of the rotatable exo-cyclic groups on disaccharides, the multiple minimum problem is overwhelming, especially at the quantum mechanics (QM) level. Also, energy surfaces based on isolated model molecules, such as used in routine QM studies, can result in predominant hydrogen bonding effects. Such surfaces would not be expected to be predictive of solid state structures that often make inter- instead of intramolecular hydrogen bonds. When using empirical force field calculations, that problem is substantially overcome by reducing the strength of the hydrogen bonding.

We have turned to QM modeling with non-hydroxyl bearing analogs of the sugars for a potentially more satisfying solution. For example, the two glucopyranose rings of a common disaccharide, cellobiose, can be replaced by tetrahydropyran rings, or sucrose can be modeled by tetrahydropyran and tetrahydrofuran. These models retain the configuration of the glycosidic linkage and the ring geometry of the disaccharides but avoid the pitfalls of 3₁⁰ (cellobiose) or 3₁¹ combinations (sucrose) of 3-fold staggered exocyclic groups. This sacrifices correct steric size and any necessary level of hydrogen bonding but is more predictive of crystalline conformations than might have been anticipated.
These models can be inexpensively improved by adding methyl groups that take the place of primary alcohol groups in the disaccharide. Because all rotamers of the methyl group are identical there is still only one basic geometry to try for each linkage geometry. A sterically more complete model substitutes all of the hydroxyl groups with fluorine atoms. For fluorinated cellobiose, there are nine combinations of orientations for the two C6-F groups to test. Such calculations have been completed at the HF/6-31G*, B3LYP/6-31G* and B3LYP/6-31+G* levels of theory. Interestingly, fluorination destabilizes the chair form of the sugar rings but has little influence on the linkage torsional energy. Compared to the fully hydroxylated models, there is little dependence on the level of theory, lending confidence to the results.

The cellobiose-type surfaces are compared with the crystalline conformations found for a wide variety of molecules having the same glycosidic linkage. Some 41 geometries are found in the Cambridge Structural Database, including cellobiose and lactose and a number of derivatives. Also considered are hundreds of applicable geometries from crystalline complexes with proteins. Maltose type surfaces are studied with conformations from a good number of small-molecule crystal structures, as well as with a variety of cyclodextrins and cycloamyloses. Deviations of the distribution of experimental geometries from the energy minima indicate the influence of hydrogen bonding in the real structures.

**Poster A7**

Timothy J. Giese and Darrin M. York  
University of Minnesota

*Improvement of Semiempirical Response Properties by Means of Chemical Potential Equalization*

The design of new-generation semiempirical quantum models for multi-scale modeling of biological reactions is of importance to the study of the molecular mechanisms of RNA catalysis. The electronic distribution of biological molecules change in response to conformational fluctuations, interactions with proteins or nucleic acids, metal ions, small molecules, and solvent. These “nonbonded” interactions are particularly severe in the case of RNA due to its high degree of charge and inherent conformational flexibility. Thus, an accurate dynamical description of RNA depends on the ability to account for the energy of response to the environment.

In addition, conventional semiempirical quantum models lack a proper description of dispersion interactions that are important for modeling large systems, hydrophobic residues, and weakly-bonded van der Waals complexes. We have implemented a transferable charge-dependent semiempirical dispersion model that significantly improves the description of dispersion forces between molecules. This work represents a first step toward the design of new efficient semiempirical quantum models with improved response properties and intermolecular interactions modeled without extending the minimal atomic orbitals basis.

**Poster A8**

George A. Hagedorn  
Virginia Polytechnic Institute and State University

*Non-Adiabatic Scattering Wave Functions in a Simple Born-Oppenheimer Model*

We describe recent mathematical results, obtained in collaboration with Professor Alain Joye, that concern non-adiabatic transitions in a simple molecular dynamics model. We study scattering theory for the time-dependent molecular Schrödinger equation

\[
i \frac{\hbar}{2} \frac{\partial^2 \psi}{\partial t^2} = -\frac{\hbar^2}{2} \frac{\partial^2 \psi}{\partial x^2} + h(x) \psi
\]
in the small $\epsilon$ (Born–Oppenheimer) limit. We assume the electron Hamiltonian $h(x)$ has finitely many levels and consider the propagation of coherent nuclear states with sufficiently high total energy. We further assume two of the electronic levels are isolated from the rest of the electron Hamiltonian’s spectrum and have an avoided crossing with a small $\epsilon$-independent gap. We compute the leading order behavior for the nuclear wave function associated with the non-adiabatic transition that is generated as the nuclei move through the avoided crossing.

This component is of order exp $(-C/\epsilon^2)$. It propagates asymptotically as a free Gaussian in the nuclear variables, and its momentum is shifted. The total transition probability for this transition and the momentum shift are both larger than what one would expect from a naive approximation and energy conservation.

**Poster A9**

Seon Ho Kim and Yongho Kim  
Kyung Hee University, Korea

**Direct Dynamics Calculations for Multiple Proton Transfer in ClONO$_2$ + (H$_2$O)$_n$, n = 1, 2**

The heterogeneous reaction of ClONO$_2$ with H$_2$O on polar stratospheric clouds has attributed to ozone hole in the poles, so the reaction of ClONO$_2$ with H$_2$O on water clusters has been investigated extensively by many scientists. The structure of hydrogen-bonded complexes and energetics of the proton transfer in ClONO$_2$ + (H$_2$O)$_n$, n = 1, 2, have been calculated at the MP2/6-31G(d,p) level. The direct *ab initio* dynamics calculation was performed at the same level. This study shows that the reaction occurs concertedly but protons and chlorine move asynchronously. Rate constants and kinetic isotope effects have been calculated by the canonical variational transition state theory with small curvature tunneling corrections. Kinetic isotope effects and tunneling coefficient have been obtained, and the results will be presented.

**Poster A10**

Hai Lin and Donald G. Truhlar  
University of Minnesota

**Redistributed Charge and Redistributed Charge and Dipole Schemes in Combined Quantum Mechanical and Molecular Mechanical Calculations**

Two schemes, namely the redistributed charge (RC) scheme and the redistributed charge and dipole (RCD) scheme, are introduced to handle link atoms for combined quantum mechanical and molecular mechanical (QM/MM) calculations, in which the QM/MM boundary passes through a covalent bond. In both schemes, the point charge at the MM boundary atom that is replaced by the link atom is redistributed to the mid-point of the bonds that connect the MM boundary atom and its neighboring MM atoms. These redistributed charges serve as classical mimics for the auxiliary orbitals associated with the MM host atom in the generalized hybrid orbital (GHO) method. In the RCD scheme, the dipoles of these bonds are preserved by further adjustment of the values of the redistributed charges. The treatments are justified as classical analogs to the QM description, and the methods are formulated in algorithms that makes them easy to incorporate in a general way in electronic structure packages. The new methods are compared quantitatively to three similar methods that were suggested by previous work, namely a charge shift scheme and two scaled charge schemes, as well as to the mechanical embedding scheme. Reasonably good results were obtained by the new methods in comparison with these other methods and with full QM calculations, indicating that the redistribution of charges (or charges and dipoles) provides a practical way to handle the QM/MM boundary when it passes through a bond. An advantage of the present schemes is that they combine the simplicity of the link atom method and the robustness of the more fundamentally justifiable GHO theory.
**Poster A11**

**Maricris D. Lodriguito**, Karol Kowalski, and Piotr Piecuch  
Michigan State University

**Method of Moments of Coupled-Cluster Equations Employing the Multireference Perturbation Theory**

It has been recently reported that the failures of the standard single-reference coupled-cluster (CC) and equation-of-motion CC (EOMCC) methods in calculations involving bond breaking can be eliminated by adding noniterative corrections to CC/EOMCC energies based on the method of moments of CC equations (MMCC).[1] We explore a new class of MMCC approaches in which information about higher-order effects that are relevant to bond breaking and excited states is extracted from the low-order multireference many-body perturbation theory (MRMBPT). It is shown that the new noniterative CC/EOMCC methods, which make use of the MRMBPT wavefunctions in designing the MMCC corrections to standard CC or EOMCC energies, provide an excellent description of single bond breaking and excited states dominated by doubles. The new MRMBPT-corrected MMCC theory eliminates the failures of the popular CC/EOMCC approaches at large internuclear distances and for excited states dominated by two-electron transition without invoking the expensive steps of higher-order CC methods.


**Poster A12**

**Vanessa Audette Lynch**¹, Steven L. Mielke², and Donald G. Truhlar³  
¹University of Minnesota  
²Northwestern University

**Vibrational-Rotational Partition Functions for the Low-Frequency Torsional Modes of H₂O₂ and Its Isotopomers**

Accurate quantum mechanical vibrational-rotational partition functions are presented for H₂O₂ and its isotopomers (HOOD, D₂O₂, H₂¹⁸O₂, and H¹⁸O-OH) using an analytic potential energy surface [1] for temperatures ranging from 300 to 2,400 K by using Monte Carlo path integral calculations. The calculations employed a new enhanced-same-path extrapolation [2] of trapezoidal Trotter Fourier path integrals. The accurate partition functions are compared to the Pitzer–Gwinn approximation [3] and separable-mode approximations. The separable-mode approximations to the partition functions treat the torsion as a hindered rotor. These are the first converged quantum mechanical partition functions for a molecule with a torsion, and they can be used to test approximate methods. Five approximate hindered rotor schemes developed previously [4] are also used to treat the low-frequency torsional mode and are tested against the accurate quantal results. Recommendations on the choice of method, based on the experimental and theoretical quantities available, are given for computing the vibrational-rotational partition function for systems with low frequency torsional modes.

References:
**Poster A13**

Matthew J. McGrath  
University of Minnesota

**CP2K-MC: A Monte Carlo Approach for First Principles Simulations**

A simulation method for performing Monte Carlo simulations from first principles is presented. The Monte Carlo code is written using the energy routines from CP2K, which evaluates energies using an atom-centered primary basis set and a plane-wave auxiliary basis set. Calculations were performed using density functional theory, using the BLYP exchange/correlation functionals. Simulations on water were run in the canonical, isobaric-isothermal, and Gibbs ensembles. Final results for the canonical ensemble are shown, along with preliminary results in the isobaric-isothermal and Gibbs ensembles. The results are compared to classical simulations and experimental results.

**Poster A14(i)**

Subhash C. Basak¹, Denise Mills¹, Douglas M. Hawkins², and Hisham El-Masri³  
¹University of Minnesota, Duluth  
²University of Minnesota, Minneapolis  
³Agency for Toxic Substances and Disease Registry, Atlanta, Georgia

**Estimation of Tissue:Air Partition Coefficients: A Comparison Of Structure- and Property-Based Methods**

Tissue:air partition coefficients are important in understanding the toxicokinetics of chemicals and in developing physiologically-based pharmacokinetic (PBPK) models. Three linear regression methods were used to develop models for the prediction of tissue:air partition coefficients including fat:air, liver:air and muscle:air for male Fischer 344 rats. The models were developed with a set of 46 diverse low molecular weight volatile compounds, as well as a subset of 26 haloalkanes. Comparisons were made between models utilizing strictly structure-based descriptors and property-based descriptors including saline:air and olive oil:air partition coefficients. The results indicated that ridge regression (RR) generally outperformed principal component regression (PCR) or partial least squares (PLS) regression. The models involving structure-based descriptors were comparable to, and in some cases superior to, models utilizing property-based descriptors. Some descriptor types, including molecular weight, low-order valence connectivity indices and descriptors of cyclicity and aromaticity, were found to be important for the prediction of all three partition coefficients; while descriptors representing polarity and hydrogen bonding were important only for the prediction of liver:air and muscle:air partition coefficients.

**Poster A14(ii)**

Subhash C. Basak¹, Denise Mills¹, Moiz M. Mumtaz², and Krishnan Balasubramanian³  
¹University of Minnesota, Duluth  
²Agency for Toxic Substances and Disease Registry, Atlanta, Georgia  
³University of California, Davis; Lawrence Livermore National Laboratory; and Lawrence Berkeley National Laboratory

**Use of Topological Indices in Predicting Aryl Hydrocarbon (Ah) Receptor Binding Affinity of Dibenzofurans: A Hierarchical QSAR Approach**

Dibenzofurans are widespread environmental contaminants that are produced mainly as undesirable by-products in natural and industrial processes. The toxic effects of these compounds are thought to be mediated through binding to the aryl hydrocarbon (Ah) receptor. In this study, we have used our HiQSAR approach in the development of QSAR models to predict Ah receptor binding affinity utilizing a set of 34 dibenzofurans. Topostructural (TS), topochemical (TC), geometrical (3D), and \textit{ab initio} (sto-3g) quantum chemical indices have
been employed either alone or hierarchically in the development of the QSAR models. Results show that, for the full set, the TS and TC indices explain most of the variance in the data. The addition of 3D and quantum chemical indices results in only slight improvement in the predictive capability of QSAR models.

**Poster A15**

Subhash C. Basak, Ramanathan Natarajan, and Denise Mills  
University of Minnesota, Duluth  

*Hierarchical Quantitative Structure-Activity Relationship (HiQSAR) Studies of Mosquito Repellency of Alicyclic Carboxamides*

In the quest for finding alternatives for the most popular topical repellant, \( N,N \) Diethyl-3-methylbenzamide (DEET), development of QSAR models play a very important role because these models can be used to tailor the similarity space and select compounds from large data sets in the identification of leads. Mosquito repellency data of alicyclic carboxamides for *Aedes aegypti* and *Anopheles quadrimaculatus* are modeled by Hierarchical Quantitative Structure-Activity Relationship (HiQSAR) technique using topostructural, topochemical, geometrical, and quantum mechanical parameters. Three types of multiple regression methods namely, ridge regression, regression using principal components extracted from the independent variables, and partial least square analysis were applied. In all the three methods Topostructural parameters are found to correlate well with the time of protection and there was no improvement in the model on adding topochemical, geometrical and quantum chemical parameters. This indicates that structural factors like size and shape of the repellent is the primary factor that governs the repellency of the carboxamides.

**Poster A16**

Kim Palmo and Samuel Krimm  
University of Michigan  

*SDFF Potential Energy Functions: Theoretical Basis and Accuracy of a Non-Iterative Polarization Model*

Our spectroscopically determined force field (SDFF) methodology [1] is briefly reviewed, with emphasis on the importance of constructing physically accurate energy functions. SDFF extensions and philosophical differences with respect to standard empirical force fields are elaborated.

As part of our efforts to include many-body interactions into the force field, we have analyzed the theory of dipole polarization and derived the difference in induction energy between an iterative (self-consistent) and non-iterative (one-step) scheme [2]. We conclude that this difference is bound to be small in most cases, so that a non-iterative polarization model can be expected to give a satisfactory representation of the induction energy. This is demonstrated with examples of configurations of water molecules. Advantages of a one-step procedure are discussed.

**Poster A17**

**Jingzhi Pu, Jiali Gao, and Donald G. Truhlar**  
University of Minnesota

**Generalized Hybrid Orbital (GHO) Method for Combined Quantum Mechanical Molecular Mechanical Calculations Based on DFT and Hybrid DFT**

In combined quantum mechanical molecular mechanical (QM/MM) calculations, the generalized hybrid orbital (GHO) method has been shown to provide a smooth connection between the QM and MM regions. The GHO method has previously been developed for semiempirical molecular orbital methods, for ab initio Hartree-Fock wave functions, and for the self-consistent-charge density-functional tight-binding theory. In the present work, we formulate the GHO algorithm and its analytical gradients based on density functional theory and hybrid density functional theory [GHO-(H)DFT]. In the proposed GHO-(H)DFT method, auxiliary charge densities are included into the calculation of the total electron density. The orthonormal constraint involving auxiliary Kohn-Sham orbitals is satisfied by carrying out a generalized hybridization based on a set of Löwdin symmetrically orthogonalized atomic basis functions. Analytical gradients are formulated for GHO-(H)DFT by incorporating additional forces associated with the GHO basis transformation. Scaling integral parameters are introduced and optimized to improve geometries near the QM/MM boundary. The GHO-(H)DFT/MM method is tested for molecular geometries and population charges of a set of small molecules and for the rotational barrier along the central C–C bond in n-butane. Proton affinities for a set of alcohol, amine, thiol, and acid are calculated by GHO-(H)DFT/MM, and compared to fully QM results. The proposed method is further applied to study the conformational energies of alanine dipeptide. Finally, we test the method for the reaction barrier height of transferring a hydrogen atom between two hydrocarbon fragments.

**Poster A18**

**J. J. Ruiz-Pernía¹, S. Ferrer¹, I. Tuñón¹, S. Martí², and V. Moliner²**  
¹Universitat de Valencia  
²Universitat Jaume I

**Potentials of Mean Force Using Interpolated Corrections in One or Two Dimensions**

Potentials of Mean Force for very large systems can be obtained using hybrid QM/MM methodology. However, in most cases, the quantum mechanical level used for the QM subsystem must be quite low, because of computational limitations. Following the ideas of Professor Truhlar, we recently proposed the application of interpolated corrections to improve the accuracy of Potentials of Mean Force obtained at semiempirical level [1]. In principle, the correction energy term is calculated as the difference between the energy obtained at a high level (HL) and a low level (LL) and is expressed as a function of the reaction coordinate followed during the simulation. In order to have a continuous and derivable function, cubic splines are used to fit this correction term.

There are several chemical processes that can not be followed using a single distinguished coordinate. Here we propose an extension of the methodology to consider the correction energy term as a function of two different coordinates. We propose two different models. In the first one the two coordinates are considered as independent and the total correction is expressed as a sum of two different cubic splines. In a second model, the correction energy term can be obtained using bicubic splines, explicitly dependent of the two considered coordinates.

**Poster A19**

Toshiyuki Takayanagi  
Saitama University, Japan

**Reduced-Dimensionality Quantum Scattering Calculations of the Reaction Between C(3P) and Acetylene**

The reaction of the ground-state atomic carbon C(3P) with acetylene has recently attracted considerable interest due to its fundamental importance in the chemistry of dense interstellar clouds. It is known that the rate constant is quite large even at low temperatures since the potential energy surface is barrierless [1]. Crossed molecular beam experiments have also been performed and it has been found that the reaction cross section is nearly proportional to $E^\alpha$ ($\alpha \sim 0.7-0.8$), where $E$ is the translational energy [1].

Although several *ab initio* electronic structure studies for understanding the reaction mechanism for C(3P) + C2H2 have been carried out so far, there exists only one dynamics study, where Buonomo and Clary report two-dimensional time-dependent quantum wave packet calculations [2]. They have considered two variables describing the position of the carbon atom with respect to acetylene. Here, we extend their calculations to include one more active degree of freedom, C-C stretching coordinate. Therefore, the problem to be solved can be reduced to a usual atom-diatom reaction system. Our three-dimensional model is rather realistic in the sense of the Born-Oppenheimer-like approximation where fast hydrogen atom motions were assumed to be adiabatic. The potential energy values in the entrance region were calculated using the hybrid density functional B3LYP method with the 6-31G(d,p) basis set using the GAUSSIAN package and a total of about 2600 points were calculated. An analytical potential energy function was then developed by a standard fitting technique.

Reactive cross sections were calculated as a function of the collision energy using the time-independent quantum reactive scattering method. The generalized $R$-matrix propagation method with an appropriate imaginary flux-absorbing potential was used. We have also employed the standard centrifugal sudden approximation neglecting Coriolis coupling terms. Details about the computational results as well as comparison to experiment will be presented at the meeting.


**Poster A20**

Keith W. Wiitala  
University of Minnesota  
Advisors: Dr. Chris Cramer and Dr. Thomas Hoye

**Empirically Derived Functionals for Predicting NMR Shifts**

A training set of 43 organic compounds and a five-factor Central Composite Design were used to optimize the parameters of the B3LYP functional for predicting NMR shifts. Total absolute errors between computed and experimental shifts were used to generate a six-dimensional response surface. Minima on these surfaces resulted in the discovery of two new NMR functionals which are more accurate than HF, B3LYP, PBE1PBE, and PW1PW91 methods for predicting training set $^{13}$C and $^1$H NMR shifts. Accuracy was further demonstrated by predicting the relative configurations of monomethylcyclohexanol derivatives.
**Poster A21**

Xin S. Zhao, J. Ilja Siepmann, and Sami Karaboni  
University of Minnesota

**Monte Carlo Investigations of the Phase Behavior of Benzene and of the Formation of Multiple Hydrates for MK-N**

Gibbs ensemble Monte Carlo simulations were used to calculate the vapor-liquid and vapor-solid coexistence curves for two simple united-atom benzene models. For both force fields the benzene molecule is modeled by six Lennard-Jones sites at the positions of the carbon atoms, but one model contains three additional sites with partial charges representing benzene’s out of plan quadrupole moment. The simulations results indicate that the model with quadrupolar interactions performs much better and predicts a triple point of benzene at $T = 254 \pm 14$ K and $p = 2.4 \pm 1.0$ kPa in satisfactory agreement with the experimental data ($T = 278.7$ K and $p = 4.785$ kPa).

Constant-stress, grand canonical and Gibbs ensemble Monte Carlo simulations were employed to study the hydrate formation for a drug molecule, MK-N. Simulations indicate the presence of multiple hydrates, including hemihydrate, dihydrate, tetrahydrate, and pentahydrate, in agreement with experiment.

**Poster A22(i)**

Sean E. Mikel and Titus V. Albu  
Tennessee Technological University

**Oxygen Reduction over Platinum: A Study of the Accuracy of Hybrid Density Functional Theory Methods**

Fuel cells transform hydrogen (or methanol) and oxygen into electrical energy reducing or eliminating the emissions problems and offering an appealing alternative to fossil fuels. Oxygen reduction is the cathodic process in fuel cells, and, in acid-based fuel cells, the desired cathodic process is the direct four-electron reduction of oxygen to water: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$. Understanding the factors influencing the kinetics of oxygen reduction over platinum and platinum alloys has been the focus of many experimental and theoretical studies in recent years.

Previous theoretical studies of outer-sphere [J. Am. Chem. Soc. 1999, 121, 11855] and Pt-catalyzed [J. Electrochem. Soc. 2000, 147, 4229] oxygen reduction using MP2/6-31G(d,p) method gave accurate activation energies results compared with experimental values but this method became prohibited as the size of the model was increased. Here we present the results of a study of the accuracy of various hybrid density functional methods for the oxygen reduction, methods that has the potential of being used successfully for larger reaction models. To determine the accuracy of each method, we determined the electrochemical potentials where the one-electron reduction of $\text{O}_2$ and one-electron oxidation of $\text{HOO}$ occur without any barrier, and we compared these results with the one obtained using MP2/6-31G(d,p) level of theory.

**Poster A22(ii)**

Sean E. Mikel and Titus V. Albu  
Tennessee Technological University

**A Hybrid Density Functional Theory Study of the Hydrogen Abstraction Reaction of Fluoromethane by the Hydroxyl Radical**

The attack by hydroxyl radical of the C–H bond in fluoromethane: $\text{OH} + \text{CH}_3\text{F} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{F}$ is an important atmospheric reaction due to an increase use of hydrofluorocarbons as substitutes to
chlorofluorocarbons. In a recent ab initio and theoretical kinetic study on this reaction, based on fitting to the experimental rate constants, Lien et al. [J. Phys. Chem. A 2001, 105, 2391] proposed an estimated barrier height of 2.8–3.2 kcal/mol for this reaction. However, this value was overestimated by all ab initio methods investigated in that study.

To complement the work of Lien et al., in this study a number of hybrid density functional theory methods have been used to calculate the barrier height for the hydrogen abstraction reaction of fluoromethane by the hydroxyl radical. The results show that some of the theoretical methods investigated here give calculated barrier heights for the hydrogen abstraction reaction that are very small. (For some methods, the barrier height is calculated to be negative!) A strong van der Waals interaction between hydroxyl radical and fluoromethane (that may be overestimated) and a small barrier height relative to this complex (barrier height that may be underestimated) are responsible for this apparent paradox. These results imply the need for a careful choice in using some of these density functional theory methods for dynamics calculations especially for reactions with small barrier height and strong interaction between reactants.

**Poster A23**

N. Kungwan and T. N. Truong*

University of Utah

**Kinetics of the Hydrogen Abstraction Reaction Class ·CH₃ + H-C(Sp³) → CH₄ + ·C(Sp³) : An Application of the Reaction Class Transition State Theory**

Kinetics of the hydrogen abstraction reaction ·CH₃ + CH₄ → CH₄ + ·CH₃ is studied by a direct dynamics method. Thermal rate constants in the temperature range of 300–2500 K are evaluated by the canonical variational transition state theory (CVT) incorporating corrections from tunneling using the small-curvature tunneling (SCT) method and from the hindered rotations. These results are used in conjunction with the Reaction Class Transition State Theory / Linear Energy Relationship (RC-TST/LER) to predict thermal rate constants of any reaction in the hydrogen abstraction class of ·CH₃ + H-C(sp³) where C(sp³) is a saturated carbon atom. Error analyses are performed and presented.

**Poster A24**

Joseph D. Scanlon and Christopher J. Cramer

University of Minnesota

**Electronic Structure of Highly Reduced Metalloccenes**

Hybrid density functional theory calculations were performed on benzyl and naphthyl transition metal metallocenes. A three by three block of transition metals were studied from Ti to W, with group 4, 5, and 6 compounds carrying an overall charge of -2, -1, and 0 respectively. Benzenes or naphthalenes in groups of two or three were used as coordinating ligands. The B3LYP level of theory was used with the Stuttgart effective core potential for metal atoms and the D95V(d) basis set for carbon and hydrogen atoms. Trends in the binding energies associated with the reaction ML₂ + L → ML₃ (M=metal and L=benzene or naphthalene) in the gas phase are discussed. Trends in the binding energies for these reactions with a solvation correction from the Born equation are also examined. The conformational preferences of the different coordination modes of the di- and tri-naphthalene complexes will also be discussed. Geometries of theoretical complexes were compared to experimental x-ray structures where available.
Poster A25

Thomas C. Allison, Carlos A. González, Ines González, Ed Lim, and Kevin Wepasnick

1 National Institute of Standards and Technology
2 University of Akron
3 Franklin and Marshall College

Hartree-Fock Dispersion for Computations on Molecular Clusters

We present a methodology to include dispersion forces in the Hartree-Fock formalism in a perturbative manner using a London dispersion term. This methodology, termed Hartree-Fock dispersion (HFD), has been used in computations on small polyatomic clusters (dimers, trimers, and tetramers) of aromatic molecules (benzene, naphthalene, and anthracene). We have coded this methodology in several popular quantum chemistry codes. The success of this formalism has suggested the replacement of the Hartree-Fock formalism by parametric Hamiltonians. This opens up the possibility of carrying out such calculations on larger clusters or in condensed phases. Results on larger clusters (up to benzene hexamers) using a semiempirical model will be presented. A new web-based database will be presented. This database contains many structures from our own calculations as well as some experimental data. One unique feature of this database is that it allows structures of atomic and molecular clusters to be uploaded for inclusion in the database. These structures are reviewed by the database maintainers and, upon approval, made generally available. It is hoped that the data collected in this database will lead to new insight into systems where long-range interactions are important to an understanding of the potential energy surface.

Poster A26

Timothy J. Dudley and Mark S. Gordon
Iowa State University

Theoretical Study of Formation and Isomerization of Al2H2 Using Multi-Reference Methods

The lowest singlet and triplet potential energy surfaces of Al2H2 have been characterized using a full-valence CASSCF wavefunction. The CASSCF geometries of minima on the singlet potential energy surface are compared to those previously reported at the B3LYP and CCSD(T) levels. Energies at the CASSCF geometries are corrected for dynamic correlation effects using MRPT and CCSD(T), with the resulting relative energy differences agreeing quite well with those obtained at CCSD(T) optimized geometries. This approach to localizing stationary points and calculating relative energies is utilized to describe isomerization pathways between the minima on the singlet surface, locate minima on the triplet potential energy surface, and characterize pathways leading to formation of bound Al2H2 species from various fragments (e.g., AlH, AlH2, Al2, and H2). Results confirm that the global minimum is the singlet dibridged isomer with other singlet isomers lying slightly
higher in energy. Though not previously analyzed, most triplet structures were found to be less than 20 kcal/mol higher in energy than their singlet counterparts. A purely attractive reaction channel, involving the insertion of H$_2$ directly into the Al-Al bond of an excited Al$_2$ species, was located and found to be exothermic by more than 40 kcal/mol. Based on energy and frequency analyses of the singlet surface, the conclusion that only the dibridged and monobridged isomers have been observed in matrix isolation experiments is suspect.

**Poster B1**

**Steven M. Bachrach**
Trinity University, San Antonio, Texas

**Solvation Effects on Nucleophilic Substitution at Sulfur**

Our extensive computational studies of gas-phase nucleophilic substitution at sulfur indicate that the reaction occurs by an addition-elimination mechanism. We have examined substitution at sulfur in sulfides, disulfides, and trisulfides in both cyclic and acyclic environments. The addition-elimination mechanism operates except in the case of strained rings, where the mechanism is $S_N^2$. We have now extended our studies to the solution phase, employing both continuum methods and incorporation of explicit water molecules. Examples to be presented include thiolate attack of cyclic and acyclic disulfides and the reaction of chloride with SCl$_2$. The addition-elimination mechanism persists in these aqueous solution cases.

**Poster B2**

**R. C. Binning, Jr.$^1$, Daniel. E. Bacelo$^1$, and Kenneth Elkner$^2$**
$^1$Universidad Metropolitana, San Juan, Puerto Rico
$^2$Cupeyville School, San Juan, Puerto Rico

**Mechanisms of Production of Cyanopolyynes Studied by ab Initio Direct Molecular Dynamics**

Cyanopolyynes, HC$_n$N, are detected in dense interstellar dust clouds. Cyanoacetylene is the most common, but molecules with as many as nine carbons have been seen. They are believed to form and grow in radical-molecule and ion-molecule reactions that have low barriers in the entrance channels. Low- or no-barrier mechanisms are necessary because the effective ambient temperatures are 50 – 100K. Some candidate reactions that have been proposed as likely in forming cyanoacetylene are:

\[
\begin{align*}
\text{CN} + \text{C}_2\text{H}_2 & \rightarrow \text{HC}_3\text{N} + \text{H} \\
\text{HCN} + \text{C}_2\text{H}_2 & \rightarrow \text{H}_2\text{C}_3\text{N}^+ + \text{H} \rightarrow \text{HC}_3\text{N} + \text{H}^+ \\
\text{N} + \text{C}_3\text{H}_1^+ & \rightarrow \text{H}_2\text{C}_3\text{N}^+ + \text{H} \rightarrow \text{HC}_3\text{N} + \text{H}^+
\end{align*}
\]

We are studying the mechanisms of these reactions by *ab initio* direct molecular dynamics to ascertain how likely they are to produce cyanoacetylene and higher polyynes.

**Poster B3**

**Yao-Yuan Chuang**
National University of Kaohsiung

**Variational Transition State Theory With Updated Hessian**

Variational Transition State Theory with Multidimensional Tunneling (VTST/MT) has been successfully used for calculating the reaction rate constants of reactions in gas and condensed phase. The Hessian updating scheme has
shown to be a useful method for providing good approximation with reduced computational costs in both geometry optimization and trajectory calculations. In this poster, we proposed to apply the Hessian updating scheme with VTST/MT for calculating the reaction rate constants of \( \text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H} \) to various reaction path following algorithms. Although we found that applying the Hessian updating scheme will not obtain a great improvement to the overall rate constants with Gradient based integrator, however, for the Hessian based integrator, it is a great help. Furthermore, as we expected, the transmission probability of the Small Curvature Tunneling theory has a great improvement as the curvature components along the reaction path are being better estimated with the updated Hessians. Even though we demonstrated this approach on a pre-fitted potential energy surface, but we believe by updating the Hessians along the reaction path will result reasonable computing costs for applying the VTST/MT calculation with \textit{ab initio} quantum chemistry software (such as GAUSSIAN and GAMESS) on computing the required energetic information in the direct dynamics scheme.

**Poster B4**

Norge Cruz Hernández and Javier Fdez. Sanz
Universidad de Sevilla

**DFT and Classical Molecular Dynamic Simulation of Gold Cluster Deposition on Rutile TiO$_2$(110) Surface**

Metal deposition constitutes one of the most appealing methods for the preparation of new materials of technological interest (catalysis, gas sensors, …). Addition of metal atoms to a surface can in principle look for different targets. Thus, a given relatively inert surface can be promoted by adding an alkali metal like Na. In another direction, specific catalysts are prepared by supporting transition metal atoms on inert surfaces. In a particular case, gold particles supported on surface oxide have been reported to be highly active especially at room temperature. In order to study such phenomenon several questions are relevant from a microscopic point of view. First we are interested by the properties of the metal surface interface: the nature of the bond, the extension of the surface reduction, etc. Secondly, we would like to know the detailed structure of the particles adsorbed at the surface. This information could help for both a better understanding of the interface and a suitable description of the active sites in a given surface reaction. As inert support we have considered the metal oxide rutile TiO$_2$(110) surface and a gold cluster of different sizes have been deposited. The interface gold-rutile was described by deposition of single Au atoms on a 2\'1 fivelayer-thick in a super-cell model. Such calculation were performed using VASP code in a periodic Density Functional Theory framework by using augmented plane-waves as wave function and only one special point in the reciprocal space. The generalized gradient approximation (GGA) of Pedew \textit{et al}. was used as density functional. In this work, with the aim of simulating a more real characteristic of the materials, including a big number of atoms, the classical dynamic simulations were done. The interaction potentials Au-Ti, Au-O and Au-Au were obtained from DFT periodic calculation using a new method of separation of the interaction of two films of atoms and the Matsui and Akaogi potential for surface. The classical simulations involved the simultaneous displacements of more than 1000 atoms including surface and adsorbed gold cluster particle. The classical simulation were performed by using DL\_POLY code.

**Poster B5**

J. Espinosa-García, J.C. Corchedo, M. Navarrete, and C. Rangel
Universidad de Extremadura

**New Hybrid Method Integrating Quantum Molecular or Molecular Mechanics Methods With Analytical Potential Energy Surfaces. Kinetics And Dynamics Applications**

The theoretical study of large polyatomic systems represents a challenge for Theoretical Chemistry, because the application of \textit{ab initio} high-level calculations is prohibitive. To circumvent this problem of large systems/high-level, DFT methods have been widely used in the literature. However, when breaking/forming bonds are
involved, transition-state zone, DFTs fail to perform well, and generally underestimate the barrier height by several kcal/mol.

An interesting and economic alternative approach to this problem is represented by the integrated methods, which describe different parts of the large system with different theoretical approaches: the “model” system, which is the more active site where the breaking/forming bonds are involved, is treated at QM high-level; and the “rest” of the system is treated at a lower-level, QM or MM. These methods are denoted as QM:QM or QM:MM combinations, respectively.

In this communication a new integrated scheme is proposed and tested, where the QM high-level description of the “model” system is replaced by an analytical potential energy surface, PES. The new scheme is denoted PES:QM or PES:MM, depending on which low-level, QM or MM, is used. Although we shall test it on a reactive system based on the reaction-path construction, and hence obtain kinetics and dynamics information, it can be applied to calculate any property for any system or compound. The hydrogen abstraction reaction $\text{CH}_3\text{CH}_3 + \text{H} \rightarrow \text{CH}_3\text{CH}_2 + \text{H}_2$ was chosen as test, because there is a lot of theoretical and experimental information (heat of reaction, activation energy, tunneling effect, rate constants, etc.) available for comparison.

Poster B6

I. García-Cruz and J. M. Martínez-Magadán
Instituto Mexicano del Petróleo

**Prediction of Benzyne-like Species in Pyrene Diradicals**

The different products that can be obtained from pyrene dehydrogenation have been studied by means of hybrid density functional theory. Most of the didehydrogenated species exhibit a diradical character. This is supported by the closeness between the geometry and energy of singlet and triplet states, and the open-shell nature of the singlet state. However, three didehydrogenated species have been found to exhibit a closed shell singlet electronic ground state. The analysis of the electronic structure, the formation energy of these didehydrogenated species and their geometrical structure reveals that these three didehydrogenated species are better described as benzyne-like moieties; two of them are of ortho- and one of meta-benzyne character. The two ortho-benzyne species have lower energies than the meta-benzyne and are favoured upon diradical formation. This interpretation is fully supported by the analysis of multiconfigurational wave functions and the order of stabilities confirmed by second order multireference perturbation theory calculations. A possible implication of the reactivity of these benzyne-like species in asphaltene formation is discussed.

Poster B7

Dave Giesen
Kodak

**MIDI! – The Little Basis Set That Can**

The MIDI! basis set was developed at the University of Minnesota as a small basis set that would give results comparable to larger basis sets. This basis set has proven quite handy as a tool for every day computation. In contrast to previously existing literature, it will be shown how small basis sets, and particularly MIDI!, can be used for computing accurate $^{13}$C NMR shifts. An example will also be given in which the potential energy surface and corresponding $^{13}$C NMR shifts computed with MIDI! were used to confirm the crystal structure of a molecule.
**Poster B8**

**Kenneth Haug, Myat Lin, and Nathaniel J. Lonergan**  
Lafayette College

*A Kinetic Monte Carlo Study of Pattern Formation in Hetero-Epitaxial Growth Comparing Cu/Ni and Pt/Ni Growing on Ni (100)*

The surface patterns formed during Cu/Ni and Pt/Ni heteroepitaxy have been investigated by kinetic Monte Carlo (KMC) simulations of the growth process at various coverages of the metals, various deposition rates, and various temperatures. Both 2-d (monolayer) and 3-d (multilayer) growth regimes are examined by KMC simulations based upon a set of rate constants consisting of 1,458 uncorrelated Cu (or Pt) and Ni atom site-to-site hopping mobilities in 2-d, supplemented by an additional set of 448 hopping mobilities for step-edge processes in the multilayer simulations. The rate constant activation energies are determined by classical-potential total-energy calculations using embedded atom potentials from the literature. General features of the surface growth are related to interaction energy differences in Ni-Cu and Ni-Pt bonding and also in mobility rate differences for the adatoms. For example we find that diffusion of Cu adatoms occurs at a faster rate, and Pt at a slower rate, than do Ni adatoms on the flat Ni(100) surface and the initial nucleation and final growth patterns of islands varies as a consequence. The final island morphologies develop to a great extent as kinetically controlled structures and they differ substantially from case to case over time periods that are long on the deposition time scale. Therefore the island pattern differences can become frozen in place resulting in interfaces with varying electronic, magnetic, and catalytic properties.

**Poster B9(i)**

**Kyung Hyun Kim and Yongho Kim**  
Kyung Hee University, Korea

*Is There Basis Set Superposition Error in Multilevel Methods? A Test on the H$_2$O and HF Dimer*

The basis set superposition error (BSSE) is often very important in the accurate calculation of dimerization energies. Accurate prediction of thermochemical properties requires appropriate consideration of the basis set incompleteness error. Multilevel methods introduced adjustable parameters to reproduce experimental data, i.e., the higher level correction (HLC) in G3 and adjustable coefficients in the MCCM. However, the HLC term is canceled out in the dimerization energy and the adjustable coefficients in the MCCM do not remove the BSSE completely. We have calculated the BSSE involved in the multilevel methods using Boys-Bernardi correction including the fragment relaxation energy. The H$_2$O and HF dimer systems were used as a test case.

**Poster B9(ii)**

**Kyung Hyun Kim and Yongho Kim**  
Kyung Hee University, Korea

*Quantum Mechanical Studies for Proton Transfer in Hydrated BH$_5$ Clusters.*

The existence of BH$_5$ was postulated on the basis of experimental observations of the acidolysis of BH$_4^-$ in aqueous solution, H$^+$ + BH$_4^-$ + 2H$_2$O $\rightarrow$ 4H$_2$ + B(OH)$_3$. In this work, we have performed quantum mechanical calculations for proton transfer in hydrated BH$_3$ clusters. Structures have been optimized at the BLYP/G3LARGE level and the energy have been calculated at MCCM-UT-MP4SDQ. Up to 5 H$_2$O molecules were added to make hydrated BH$_3$ cluster systems. The BH$_5$ cluster with 4 water molecules has the lowest barrier of proton transfer, which is 1.27 kcal/mol. This energy barrier is comparable to the activation energy of aqueous proton transfer estimated from NMR relaxation time experiments.
**Poster B9(iii)**

**Kyung Hyun Kim** and **Yongho Kim**
Kyung Hee University, Korea

**Theoretical Study for the Lewis Acid-Base Interaction and Weak Hydrogen Bonding in CO$_2$-Philic Molecules**

Supercritical CO$_2$ has become one of the most important topics in the coming decades in relation to clean and environmentally benign chemistry and technology. The development of CO$_2$-soluble molecules has recently been a kernel of “green” chemistry. Lewis acid–base interaction and C-H--O weak hydrogen bonding were suggested to be important to the solubility of CO$_2$-philic molecules. We have calculated structures and energies for CO$_2$ complex of various organic molecules at the MP2/6-31+G(d), MCG3 and the MCCM-UT-CCSD levels. Our results show that the Lewis acid–base interactions in CO$_2$-philic molecules is much stronger than the C-H--O weak hydrogen bonding. The weak hydrogen bonding might provide a cooperative effect to the solubility of CO$_2$-philic molecules.

**Poster B10**

**Tiqing Liu** and **Patrik R. Callis**
Montana State University

**Quantitative Prediction of Fluorescence Quantum Yields for Tryptophan in Proteins**

Variation of intrinsic tryptophan (Trp) fluorescence intensity and lifetime in proteins is widely exploited to follow changes in protein structure such as folding/unfolding, substrate or ligand binding, and protein-protein interactions. Although a credible candidate for the source of weak Trp fluorescence in some proteins has long been believed to be electron transfer from excited Trp to an amide carbonyl group, recognition of when such a process should be exceptionally efficient has not been possible. Here we propose a reasonable basis for the 30-fold variation by the use of quantum mechanics-molecular mechanics simulations in which the energy of the lowest Trp ring-to-amide backbone charge transfer (CT) state is monitored during dynamics trajectories for 24 Trps in 17 proteins. The energy, fluctuations, and relaxation of high lying CT states are extremely sensitive to protein environment (local electric field direction and strength). The quantum part is N-formyltryptophanamide (NFTA, an indole ring plus two amide groups) for predicting quenching by local amides, and is extended as a supermolecule consisting of NFTA and another quenching group (amides in side chains of residues Gln and Asn, imidazole in histidine, and dimethyl disulfide in a disulfide bond). Application of basic electron transfer theory with a single empirical electronic coupling reveals that the entire 30-fold range is explainable from local electric field effects on electron transfer to a nearby amide or other acceptors. A semi-quantitative prediction using only average energy gap and variance was achieved by using a universal electronic coupling constant and energy offset. A key new concept uncovered in this work is that charged groups near the Trp can have profound effects on fluorescence lifetime and quantum yield—but location is critical. Negative (positive) charge will decrease (increase) quantum yield if closer to the indole ring than to the electron acceptor because these arrangements stabilize (destabilize) the CT state. If the negative charge is closer to the acceptor, the opposite will be true.
Pseudorotation of Natural and Chemically Modified Biological Phosphoranes: Implications for RNA Catalysis

Pseudorotation reactions of biologically relevant oxyphosphoranes were studied using density functional theory and continuum solvation methods. A series of 16 pseudorotation reactions involving acyclic and cyclic oxyphosphoranes in neutral and monoanionic (singly deprotonated) forms were studied, in addition to pseudorotation of PF$_5$. The effect of solvent was treated using three different solvation models. The barriers to pseudorotation ranged from 1.5 to 8.1 kcal/mol and were influenced systematically by charge state, apicophilicity of ligands, intramolecular hydrogen bonding, cyclic structure and solvation. Barriers to pseudorotation for monoanionic phosphoranes occur with the anionic oxo ligand as the pivotal atom, and are generally lower than for neutral phosphoranes. The OCH$_3$ groups were observed to be more apicophilic than OH groups, and hence pseudorotations that involve axial OCH$_3$/equatorial OH exchange had higher reaction and activation free energy values. Solvent generally lowered barriers relative to the gas phase reactions. These results, together with isotope $^{18}$O exchange experiments, support the assertion that dianionic phosphoranes are not sufficiently long-lived to undergo pseudorotation. Comparison of the density-functional results with those from several semiempirical quantum models highlight a challenge for new-generation hybrid quantum mechanical/molecular mechanical potentials for non-enzymatic and enzymatic phosphoryl transfer reactions: the reliable modeling of pseudorotation processes.

Results of further study of pseudorotation reactions of thiophosphorane molecules that serve as model intermediates in chemically modified RNA transphosphorylation are presented. These results, together with results for in-line nucleophilic attack, provide detailed insight into biological phosphorous reactivity, and in particular, the rates and pH dependence of transphosphorylation, including the nature of thio effects, in RNA systems.

Molecular Dynamics Simulation of the N-Terminal Auto-cleavage of SARS-CoV Main Proteinase

Severe acute respiratory syndrome coronavirus (SARS-CoV) has been identified as the causative agent of SARS. Like other 3C-like human coronavirus main proteases, the SARS-CoV main proteinase plays an important role in mediating viral replication and transcription functions through extensive proteolytic processing of two overlapping replicase polyproteins, pp1a and pp1ab. Therefore, understanding the proteolytic process by SARS-CoV main proteinase will help successful inhibition of this enzyme and treatment of SARS.

SARS-CoV main proteinase is a member of cysteine proteases with a Cys-His active site dyad. Starting from the X-ray crystal structure of SARS-CoV main proteinase determined at pH 7.6 (which is an optimal pH for SARS-CoV main proteinase activity), we carried out molecular dynamics simulations using a combined QM/MM method on its N-terminal auto-cleavage catalysis (substrate: H$_2$N-Thr-Ser-Ala-Val-Leu-Gln↓Ser-Gly-Phe-Arg-COOH, the cleavage site is Gln↓Ser). The 2-dimensional potential of mean force along the whole reaction pathway has been computed, and it shows that the acylation step is rate-limiting with a combination of concerted (reactant and product state regions) and step-wise (transition state region) mechanism, whereas the deacylation step is a well concerted process. In this presentation, the catalytic mechanism of SARS-CoV main proteinase will be discussed in detail.
Carbon Nanotube Fracture Strengths—The Real Explanation for the Theoretical/Experimental Discrepancies

Quantum mechanical (QM) estimates of the fracture strength of carbon nanotubes (CNTs) range from 75 to 135 GPa whereas the experimental measurements range from 11 to 63 GPa. The conventional explanation for this discrepancy is that aggregation of stress-induced Stone–Wales defects leads to a local weakening of the tube and ultimately initiates fracture. Our QM calculations show that such aggregations do not substantially weaken CNTs, although certain widely used empirical bond-order potentials erroneously predict that they do. Instead, we demonstrate that the experimental results can be explained by the presence of holes introduced by the use of harsh oxidative purification processes. We also explore the effect that other types of defects and chemical modifications have on CNT mechanical properties.

An Efficient Linear-Scaling Ewald Method for Long-Range Electrostatic Interactions in Combined QM/MM Calculations: A Development and Its Comparisons With Spherical Cut-offs Method

In order for an efficient evaluation of long-ranged electrostatic forces during molecular dynamics, an extension of Ewald summation method in the scheme of combined QM/MM method employing semiempirical Hamiltonian is presented. The method is based on splitting of total Ewald potential into short-range interaction and long-range pair-wise periodic correction that interacts with electrons and nucleus at quantal atom sites under monopolar approximations and on the Mulliken charge representation of QM charge distribution in image cells. The implementation and performance of current method is tested by computing potential of mean force (PMF) under periodic boundary molecular dynamics (PBMD) simulations in a series of simulations of the ionic association of 1) ammonium chloride and 2) ammonium metaphosphate, and the dissociative phosphoryl transfer mechanism of 3) methyl phosphate and 4) acetyl phosphate. The computed PMFs are compared with the corresponding PBMD simulations using electrostatic cut-offs, and with results from non-periodical stochastic boundary molecular dynamics (SBMD) simulations, with electrostatic cut-offs and with full electrostatics.

Phosphate Hydrolysis in Solution and the Transphosphorylation in Phosphoglucomutase

Enzyme-catalyzed phosphoryl transfer reactions often involve the nucleophilic attack of acidic amino acids, such as aspartic and glutamic acid, to phosphates. In the present work, hybrid density-functional calculations are performed to characterize the reactivity of phosphate diesters to nucleophilic attack by acetate. The influence of charge/protonation state and of phosphate ring structure are considered on the reaction path and free energy barriers. The effect of solvation is considered using several implicit solvation models including the PCM, and a variant of the COSMO-RS models. These data provide insight into the factors that govern biological phosphate reactivity and provide benchmark data for design of improved semiempirical quantum models for phosphate hydrolysis reactions. Calculations on the active site of phosphoglucomutase, the first enzymatic structure for
which an unmodified catalytic intermediate has been trapped by X-ray crystallography, provide insight into the reaction free energy profile and stability of the intermediate. It is expected that these calculations, together with experimental data will provide a detailed insight and contribute to a better understanding of the mechanisms of phosphoryl transfer in this important set of enzymatic reactions.

**Poster B16**

Qi Wang and Yuan-Ping Pang  
Mayo Clinic College of Medicine

**3D Model of a Truncated-Cofactor-Bound Serine Protease of West Nile Virus NS3 Predicted by Multiple Molecular Dynamics Simulations**

West Nile virus (WNV) infection has recently become a big health concern in the United States. The NS3 serine protease (NS3P) of WNV plays a crucial role in viral replication and has unique substrate specificity, so it has been identified as a target for structure-based design of anti-WNV agents. Experiments show that the active form of the enzyme is a heterodimer of NS3P in complex with a cofactor. Currently X-ray or NMR structures of apo NS3P and its cofactor-bound complex are unavailable. Here we report a 3D model of NS3P in complex with a cofactor fragment developed by homology modeling and refined by 400 different molecular dynamics simulations (2.0 ns for each simulation with a 1.0-fs time step). The 3D model suggests that cofactor binding facilitates the formation of an oxyanion hole that comprises the amide protons of Gly133 and Ser135. The model lays the foundation of further work on anti-WNV drug design.

**Poster B17**

Neeraj Rai and J. Ilja Siepmann  
University of Minnesota

**Extending the Transferable Potentials for Phase Equilibria Force Field to Aromatic Heterocycles and Investigating Polymorphism in ROY**

Polymorphism plays an important role in many industrial applications such as pharmaceutics and fat-based food products. A good force field is very crucial for predicting polymorphism in molecular crystals. To this end we have extended the transferable potential for phase equilibria (TraPPE) force field to nitrogen containing aromatic heterocycles, e.g., pyridine and pyrimidine. Monte Carlo simulations in the canonical Gibbs ensemble were carried out to determine the parameters that reproduce the critical temperature and saturated liquid densities. For pyridine the TraPPE-UA model gives more accurate results than the OPLS-AA model despite less computational cost for the former model. In order to see the efficacy of molecular simulations in predicting polymorphism we have carried out constant-stress simulations for 5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile (ROY). We have used two different sampling approaches either treating ROY as totally rigid or allowing torsional flexibility to see how conformational freedom affects the stability of the different polymorphs of ROY. The simulations predict different stability order than experiment which indicates the challenges in polymorph prediction.
**Poster B18**

Marcel Schmidt am Busch and Ernst-Walter Knapp  
Free University of Berlin

**Accurate pKₐ Determination for a Heterogeneous Group of Organic Molecules**

Single molecule studies to compute pKₐ values, proton affinities (gas phase acidity/basicity) and the electrostatic energy of solvation have been performed for a heterogeneous set of 26 organic compounds. Quantum mechanical density functional theory (DFT) using the Becke-half&half and B3LYP functionals on optimized molecular geometries to investigate the energetics of gas phase protonation have been carried out. The electrostatic contribution to the solvation energies of protonated and deprotonated compounds were calculated by solving the Poisson equation using atomic charges generated by fitting the electrostatic potential derived from the molecular wave functions in vacuum. The combination of gas phase and electrostatic solvation energies by means of the thermodynamic cycle enabled us to compute pKₐ values for the 26 compounds, which cover six distinct chemical groups (carboxylic acids, benzoic acids, phenols, imides, pyridines and imidazoles). The computational procedure to determine pKₐ values is accurate and transferable with a root mean square deviation of 0.53 and 0.57 pKₐ units and a maximum error of 1.0 pKₐ and 1.3 pKₐ units for Becke-half&half and B3LYP DFT functional, respectively.

**Poster B19**

Xuelin Wang and Angela K. Wilson  
University of North Texas

**An Examination of Functional Performance With Respect to Basis Set**

Density functional theory has been used in combination with the correlation consistent and polarization consistent basis sets to investigate the structures and energetics for a series of first row closed shell molecules of potential importance in atmospheric chemistry. The impact of basis set choice upon molecular description has been examined, and irregular convergence of molecular properties with respect to increasing basis set size for several functionals and molecules has been observed. We examine possible reasons and solutions for this unexpected behavior.

**Poster B20**

Hong Wu and Rainer Glaser*  
University of Missouri-Columbia

**Anisotropic Effects of the DNA Environment on Nitrosative Nucleobase Deamination. A Combined ab Initio and Molecular Dynamics Study**

Genomic stability and its maintenance is the key prerequisite for good health. Nitrosation is a key endogenous cause for oxidative DNA damage and we are studying the chemical mechanisms leading to the carcinogenesis. It is our central hypothesis that 5-cyanoimino-1H-imidazole-4-oxomethylene is formed by nitrosative deamination of guanosine (dGuo) with concomitant pyrimidine ring-opening and that subsequent 1,4-addition of water leads to 5-cyanoamino-1Himidazole-4-carboxylic acid (CAICA). CAICA is the precursor for formation of oxanosine (dOxo) and our recent $^{18}$O-labeling studies of guanosine deamination fully support this hypothesis (JACS 2004, 126, 9960). The interpretation of the isotopomer ratio ($^{18}$O6 vs. $^{18}$O7) in dOxo requires the knowledge of the rotational barrier about the C-COOH bond in CAICA. A low rotational barrier assures an equal distribution of $^{18}$O between both acid O-atoms and an isotopomer ratio of unity. On the other hand, a high rotational barrier would give rise to an isotopomer ratio that differs from unity. Here, we present the results of ab initio and
molecular dynamics studies that show large increases of the rotational barrier in the DNA environment as the result of the interaction of CAICA with neutral or protonated cytosine.

Poster B21

Yan Zhao, Benjamin J. Lynch, and Donald G. Truhlar
University of Minnesota

Multi-Coefficient Extrapolated Density Functional Theory for Thermochemistry and Thermochemical Kinetics

We have developed a new kind of multi-coefficient correlation method (MCCM) by empirically mixing correlated wave function methods and density functional methods. The new methods constitute a generalization of hybrid density functional theory and may be called multi-coefficient extrapolated density functional theory. Results by the new methods are compared to those obtained by G3SX, G3SX(MP3), CBS-Q, and MCCM/3 for the calculation of atomization energies, barrier heights, ionization potentials, and electron affinities. These results show that the multi-coefficient extrapolated density functional theory is more accurate for thermochemistry and thermochemical kinetics than the pure wave function methods of comparable cost.

Poster B22

Carolina M. A. Rio and J. Brandão
Departamento de Química e Bioquímica, Faculdade de Ciências e Tecnologia, Universidade do Algarve, Campus de Gambelas, 8005-139 Faro, Portugal

The Dynamics of the Reaction Between O (1D) and DH and the Isotopic Effect

The reaction O(1D) + H₂ → OH + H and its isotopic variants plays an important role in atmospheric chemistry and also is important in combustion chemistry. It has been taken as a prototype for insertion reactions. As a result, it has been subject of several experimental studies. Also theoretical studies of its dynamics have been carried out. In absence of energy barrier, the long-range interactions [1] between
reactants should play an important role on the dynamics of the reaction of \( \text{O}(^1\text{D}) \) with \( \text{H}_2 \) that mainly occurs in the ground state potential energy surface for \( \text{H}_2\text{O} \) [2]. Quasiclassical and capture studies [3] on a new potential energy surface that carefully reproduces these interactions are in close agreement with the most recent estimates for the thermal rate constant, when the effects of the excited surfaces is taken into account.

The isotope effect in these reactions is an additional test to the accuracy of the potential energy surface. In this work we study the dynamics of the \( \text{O}(^1\text{D}) + \text{D} \text{H} \) reaction at fixed collision energies [4] using quasiclassical trajectory calculations on a double-valued potential energy surface for \( \text{H}_2\text{O} \) [2]. In order to compare with experiment we have carried out quasiclassical trajectories calculations on \( \text{O}(^1\text{D}) + \text{D} \text{H} \) reaction at the fixed translational energies of 2.05, 3.7, and 4.55 kcal mol\(^{-1}\). In particular, we analyse the reactive cross section, the opacity function, and the differential cross sections. In this work we also study the energy distribution of the products for the \( \text{O}(^1\text{D}) + \text{D} \text{H} \) reaction. We also analyse the H/D ratio, \( \Gamma_{\text{H}/\text{D}} \), where there are larger divergences between the results from different potential energy surfaces and experiment. The agreement found between our QCT results [3,4,5] and experiment reinforces the accuracy of the \( \text{H}_2\text{O} \) potential energy surface used.

This work was supported by:
- FCT under the POCTI/CTA/41252/2001 research project, co-financed by the European community fund, FEDER.
- Centro Multidisciplinar de Química do Ambiente (CMQA).

References:

**Poster B23**

Shikha Nangia,* Ahren W. Jasper, and Donald G. Truhlar

**Army Ants Algorithm for Efficient Trajectory Surface Hopping Calculations on Chemical Systems With Coupled Electronic States**

Semiclassical trajectory surface hopping calculations on systems with coupled electronic states involve propagation of an ensemble of independent classical trajectories that make instantaneous transitions (hops) between electronic states. Tully proposed the fewest-switches method for surface hopping calculations using either of two very diverse sampling schemes, namely the anteater algorithm and the ants algorithm. However for systems with very weakly coupled electronic states, the hopping events are rare, and both the anteater and ants algorithms are inefficient and computationally expensive. The army ants algorithm provides a form of a rare event sampling scheme for increasing the efficiency of the calculations and is applicable for systems with any strength of coupling. The efficiency of is controlled by an input parameter, and by using an optimal value of the parameter the algorithm may be used to sample events with very low probabilities on the order of \( 10^{-8} \). The currently available algorithms would require an enormous amount of computational effort to sample such infrequent events, e.g., \( \sim 10^{-10} \) hours running in parallel on four processors whereas the army ants algorithm can obtain converged results in \( \sim 10 \) hours. The input parameter in the army ants algorithm allows flexibility in the algorithm and it can be reduced to the anteater and ants schemes if desired for specific applications. The efficiency of the army ants algorithm makes it the method of choice for systems with low-probability events. The army ants
algorithm has been successfully applied to a model system involving atom-diatom scattering event and has shown excellent agreement with the quantum mechanical dynamical calculations.

**Poster B24**

**Wenli Wang**, Carla J. Rosa, C. F. N. F. Mogo, B. C. N. da Silva, and J. Brandão  
Universidade do Algarve

**Quantum and Classical Studies of the \( \text{O}^3\text{P} \) + \( \text{H}_2 \rightarrow \text{OH} + \text{H} \) Reaction**

The reaction \( \text{O}^3\text{P} \) + \( \text{H}_2 \rightarrow \text{OH} + \text{H} \) is known to be a major participant in combustion processes and is of importance in atmospheric reactions as the OH radical produced is a reactive species in ozone chemistry. It is also important from a dynamics perspective because the reaction is a prototype for hydrogen-atom abstraction reactions and can be used for studying the intersystem crossing effects in the gas phase bimolecular reaction dynamics. Recently the title reaction has been the focus of experimental and theoretical works[1-3].

For the theoretical studies of reaction dynamics of the title reaction, potential energy surfaces (PESs) of chemical accuracy are needed. Recently we reported [4] a new global PES for the lowest \( ^3\text{A}'' \) electronically adiabatic state of \( \text{O}^3\text{P} \) + \( \text{H}_2 \) using the Double Many-body Expansion (DMBE) method. The long-range interactions are modelled using the Slater-Kirkwood expression from the \textit{ab initio} polarizabilities of the different fragments according to the restrictions of symmetry and spin conservation contained in the Wigner-Eitmer rules. High quality \textit{ab initio} energies at different geometry needed to fit this potential energy surface were obtained from authors of ref.1 and calculated by us in part.

Using the new potential energy surface, we present results of time-dependent quantum mechanics (TDQM) and quasiclassical trajectory (QCT) studies for the title reaction. The calculated cross sections and relevant dynamic details are compared with the experimental results and other theoretical results with different PESs.

This work was supported by:
- FCT under the POCTI/CTA/41252/2001 research project, co-financed by the European community fund, FEDER.
- Centro Multidisciplinar de Química do Ambiente (CMQA).

References:

**Poster B25**

**Li Sun**\(^1\), J. Ilja Siepmann\(^1\), Wendy L. Klotz\(^2\), and Mark R. Schure\(^2\)
\(^1\)University of Minnesota  
\(^2\)Rohm and Haas Company

**Simulating gas-liquid retention in polar stationary phases**

Con gurational-bias Monte Carlo simulations in the isobaric-isothermal Gibbs ensemble were carried out to investigate the chromatographic partitioning of a diverse set of solutes in polar stationary phases. In these simulations, the united-atom version of the transferable potentials for phase equilibria (TraPPE-UA) force field was used to model all solutes, stationary phase solvents and helium. As a starting point, the partitioning of primary and secondary alkanols and normal alkanes between a dioctylether phase and a helium vapor phase was investigated. The Kovats retention indices, and the absolute and relative free energies of transfer and partition
coefficients were calculated at four different temperatures ranging from 303.15 K to 348.15 K. The enthalpies and entropies for hydrogen bond formation were also calculated from the temperature-dependence of the equilibrium constants for hydrogen-bond formation. The importance of hydrogen-bonding for the separation factor of the primary and secondary alkanol decreases substantially with increasing temperature. As a step up, the partitioning of three normal alkanes, five primary and secondary alkanols, and three alkyl ethers between a helium vapor phase and a polyethylene oxide stationary phase (MW = 382 g/mol) was studied at two different temperatures, 353.15 K and 393.15 K. The results are in good agreement with experimental values. Analysis of the microscopic structure of the retentive phase indicates that the contribution of hydrogen bonding to retention is of the same magnitude for all primary alkanols, but is smaller for the secondary alkanol, and the influence of the polarity of the carbowax phase is substantially smaller for the alkyl ethers.

Poster B26

Jana Khandogin and Charles L. Brooks, III
The Scripps Research Institute
A New Approach to Include Proton Tautomerism in Constant-pH Molecular Dynamics Simulations

Molecular simulations of pH-dependent biological phenomena require dynamical control of the protonation states. In recent years, several constant-pH molecular dynamics techniques have emerged. This presentation will focus on a molecular dynamics technique with continuous titration coordinates based on the dynamics and Generalized Born solvation methods. Current effort involves the development of a new model that includes proton tautomerism in groups containing multiple titration sites. In this model, a new dynamic variable is introduced to represent the tautomer conversion coordinate, in addition to the variable that represents the titration degree of freedom. The non-bonded and electrostatic solvation energies are attenuated by both and variables. So is the pH-dependent biasing potential that gives rise to the relative protonation free energy. The model potential that corrects for the arbitrary classical description of the titration pathway is a forth-order polynomial in terms of and, and degenerates to a quadratic function if either protonation or tautomeric state is fixed. The model potential has been analytically derived for two types of titration groups: one with the deprotonated tautomeric states, such as His, and the other with the protonated tautomeric states, such as Asp or Glu. In this presentation, we will discuss the test results and an application to the conformational dynamics of amyloid (1-28) peptide under different pH conditions.

Poster C1

Divesh Bhatt, J. Ilja Siepmann*
University of Minnesota
Computational Investigation of the Stability of n-Propylbenzene Polymorphs

Polymorphism in n-propylbenzene is investigated using a variety of computational techniques. Polymorph Predictor (PP), a commercial software, can be used to predict possible polymorphic structures in different space groups and ranks them according to their minimized lattice energies. Two different molecular mechanics force fields (COMPASS and Dreiding) were used and result in a different stability ranking for the crystal structures and space groups. For example, the COMPASS force field predicts that a crystal structure with space group P21/c is most stable, whereas, the Dreiding force field yields a crystal in the space group C2c. In addition, the lattice energies of all were computed using the TraPPE (Transferable Potentials for Phase Equilibria) force field, and a surprisingly low correlation of the lattice energies and stability rankings is observed.

The lattice energies obtained above only reflect the relative stability of the crystal structures at 0 K. Thus, constant stress-isothermal Monte Carlo simulations (1 bar, 170 K) of the crystal structures were performed starting from the 0 K lattice structures. The ranking of the enthalpies of the crystal structures was found to be substantially different than for the lattice energies, thereby suggesting that lattice energies are a poor indicator for relative polymorph stability. Additionally, Gibbs Ensemble Monte Carlo (GEMC) simulations were employed to
investigate the solid-vapor phase equilibria and to rank the different polymorphs in order of their free energies that can be obtained from the saturated vapor pressures.

*Author for correspondence. e-mail: siepmann@chem.umn.edu

**Poster C2**

Edward A. Boudreaux and Eric Baxter
University of New Orleans

**A Study in the Dynamics of Formation and Properties of Cr2 And Mo2 From Their Respective Atoms Ulations via the SCMEH-MO Method.**

The SCMEH-MO method of molecular orbital calculations has enjoyed some 25 years of development and applications, with amazing success in a wide variety of molecular systems. This presentation addresses the dynamics of formation and bonding in two molecules which have proven to be great challenges to “state of the art” methods of computational quantum chemistry.

It is shown, for what appears to be the first time, that both valence and valence-core electrons are involved in the formation and equilibrium bonding stabilities of Cr2 and Mo2. Both the theoretical foundation and the unique conditions for the manifestation of these effects are the topics of substance for this presentation.

**Poster C3(i)**

N. Balucani¹, D. Skouteris¹, G. Capozza¹, E. Segoloni¹, P. Casavecchia¹, M. H. Alexander², G. Capecchi³, and H.-J. Werner³
¹Università di Perugia
²University of Maryland
³Universität Stuttgart

**The Dynamics of Prototype Abstraction Reactions: Crossed Beam Experiments and Exact Quantum Scattering Calculations on Coupled ab Initio Potential Energy Surfaces for the Reaction Cl(2P₃/₂,1/₂) + H₂**

Perhaps the most challenging current topic in molecular reaction dynamics is the role of nonadiabatic effects. The Cl + H₂ reaction has emerged as the most important reaction in which to understand such effects, in part because of the publication of experiments by Liu and co-workers, who conclude that the nonadiabatic Cl(2P₁/₂) + H₂ reaction possesses larger cross sections than the adiabatic Cl(2P₃/₂) + H₂ reaction [1]. This is contrary to our expectations for the importance of nonadiabatic effects in this reaction [2].

To assess the relative reactivity of the spin-orbit (SO) excited state of atomic chlorine with molecular hydrogen, we have measured differential cross sections (DCSs) at three collision energies (Eₑ = 3.85, 4.25, and 5.85 kcal/mol) using a crossed beam apparatus with mass spectrometric detection and TOF analysis and employing an atomic Cl beam with a known concentration of the ground and excited SO states, as determined from Stern-Gerlach magnetic analysis [3]. As done in previous work, where QCT and quantum (QM) scattering calculations on the ground state G3 potential energy surfaces (PES) proposed by Truhlar and coworkers were directly compared to the experimental results at Eₑ=5.85 kcal/mol [4,5], the first determination of DCSs from QM scattering calculations on a set of coupled ab initio PESs [6], after transformation into the laboratory frame and averaging over experimental conditions, are compared with the laboratory data [7]. The multi-electronic-state QM scattering prediction differs somewhat from the experimental results. This disagreement is likely due to an underestimation of the degree of rotational excitation of the HCl product, due to residual imperfections in the exit channel of the ab initio PESs. In particular, an increase in the reactivity of the excited SO state would result in poorer agreement with experiment. Consequently, the present comparison [7] does not support the conclusion, by
Liu and co-workers [1], that the title reaction is dominated by reaction of the excited spin-orbit state of the Cl atom. The need for more work, both experimental and theoretical, is clear.

Acknowledgments: This work has been carried out within the EC Research Training Network REACTION DYNAMICS (contract HPRN-CT-1999-00007).

References

Poster C3(ii)

N. Balucani¹, G. Capozza¹, E. Segoloni¹, L. Cartechini¹, R. Bobbenkamp¹, **P. Casavecchia¹**, L. Bañares²; F. J. Aoiz², P. Honvault³, B. Bussery-Honvault³, J.-M. Launay³

¹Università di Perugia
²Universidad Complutense
³Université de Rennes I

The Dynamics of Prototype Insertion Reactions: Crossed Beam Experiments Versus Quantum and Quasiclassical Trajectory Scattering Calculations on ab Initio Potential Energy Surfaces for C(¹D) + H₂ and N(²D) + H₂

In order to deepen our understanding of the dynamics of *insertion* reactions [1,2], we have recently extended our crossed beam investigations beyond O(¹D)+H₂ to two other prototypical reactions, N(²D)+H₂ and C(¹D)+H₂, which occur on a PES with a deep well associated with the strongly bound species NH₂ and CH₂, respectively. We exploit the capability of generating continuous supersonic beams of N(²D) and C(¹D) atoms [1, 2]. We have studied C(¹D)+H₂ at two collision energies, Eₖ=1.86 and 3.8 kcal/mol, and the isotopic variant C(¹D)+D₂ at Eₖ=3.6 kcal/mol by measuring product angular and velocity distributions in crossed beam experiments with mass spectrometric detection and time-of-flight analysis. The results at Eₖ=1.86 kcal/mol, which were previously compared with statistical predictions [2], have been compared with exact quantum-mechanical (QM) as well as quasiclassical trajectory (QCT) scattering calculations [3] carried on a new ab initio PES [4]. For the higher Eₖ of 3.8 kcal/mol and for C(¹D)+D₂ the experimental results have been compared with the results of QCT calculations. The *ab initio* PES has been found to give a fairly good description of the reaction dynamics of C(¹D)+H₂. The discrepancies observed between the QM results and experiment may be ascribed either to deficiencies of the long-range region of the PES or to the involvement of excited state PESs, non adiabaticic effects and intersystem crossing between the triplet and singlet CH₂ PESs.

Following on studies of the isotopic variant N(²D)+D₂ at Eₖ=15.9 and 21.3 kJ/mol, and comparisons with QCT calculations on an accurate ab initio ground state 12A" PES [5], we have investigated the reaction N(²D) + H₂(j=0-3) → NH + H, at Eₖ=15.9 kJ/mol and compared the results with those of exact QM and QCT calculations. Small but significant discrepancies between QCT and QM calculations suggest the occurrence of quantum effects—tunneling through the combined potential and centrifugal barrier, similarly to what seen for abstraction...
reactions [6]. The good agreement between QM predictions and experiment assess the quality of the \textit{ab initio} ground state PES.

Acknowledgments: Work supported by the Italian MIUR and in part by the European Commission through the Research Training Network REACTION DYNAMICS (contract HPRN-CT-1999-00007).

References


**Poster C4**

**John Cullen**

University Of Manitoba

**The Generalized Valence Bond Model Revisited**

For the study of reaction kinetics one of the simplest and fastest multiconfiguration self consistent (MCSCF) methods available is the generalized valence bond (GVB) model. When the coupled cluster approximation is applied to the GVB wave function, configuration interaction (CI) coefficients become analytic in form and the total electron correlation energy reduces to a sum of localized bond/antibond two electron CI energies. Recently we have investigated a simpler version of this theory in which localized bonding orbitals are formed from the set of unrestricted Hartree Fock (UHF) natural orbitals or some equally fast variant. The antibonding orbitals are determined with GVB. For \(N\) atomic orbitals and \(m\) GVB pairs, after an initial integral transformation step is performed, the computational storage and speed requirements are found to formally scale as \(N^2 m\) and \(N m^2\) respectively per iteration over the set of GVB pairs. To assess the accuracy and actual computational speed of this model we have carried out calculations on several moderately large molecular systems. Theory, results (including computational times) are presented and analyzed.

**Poster C5**

**Holly Freedman** and Thanh N. Truong*

University of Utah

**The Coupled RISM/Simulation Methodology and its Application to Determine Solvation Free Energies of Molecules in Aqueous Solution**

The energetics of a solvated molecular system may be significantly affected by solvent free energy contributions. We have recently proposed a new methodology for computing solvation free energies, without the need for performing free-energy simulations. In the new method, the thermochemistry of solvation can be determined from the reference interaction site model (RISM) formalism where the radial distribution functions are obtained from a simulation trajectory, instead of by simultaneous solution of the RISM and closure relations. This new methodology is quite practical, only one simulation being required, and could potentially serve as a valuable tool.
in modeling solvated macromolecules. We will discuss the coupled RISM/simulation approach, and selected results will be presented looking into the applicability of this method.

**Poster C6**

**Benjamin F. Gherman,** William B. Tolman, and Christopher J. Cramer  
University of Minnesota

**Modeling Dioxygen Activation at Monocopper Enzyme Sites**

The activation of molecular oxygen at monocopper centers plays an important role in biology, and in particular with regard to the biosynthesis of neurohormones by the Cu-containing enzymes dopamine β-monooxygenase (DβM) and the peptidylglycine α-hydroxylating monooxygenase (PHM) component of the bifunctional peptidylglycine α-amidating monooxygenase (PAM). In order to gain an understanding of the first stage of the catalysis (i.e. dioxygen activation at the monocopper active sites), 1:1 Cu/O$_2$ adducts coordinated to the biomimetic β-diketiminate and anilido-imine ligands of Tolman and co-workers[1, 2] have been studied using a combination of DFT and CASPT2 methods, a protocol which stems from earlier work on closely related systems.[3, 4] Calculations have focused on characterizing the formation of the adducts, interconversion between side-on and end-on adducts, and properties of the protonated forms of the adducts. These results[5] will form the foundation for subsequent work on O–O bond cleavage to potentially yield Cu(III)=O species as well as modeling of the hydroxylation reaction carried out by the Cu/O$_2$ adducts (i.e. the second stage of the DβM and PHM reactions).


**Poster C7**

**Brent A. Gregersen** and Darrin M. York  
University of Minnesota

**Hybrid QM/MM Calculations of Phosphoryl Transfer Reactions: Modeling the Electrostatic Environment With a New Variational Electrostatic Projection (VEP) Method**

Despite the demonstrated importance of long-ranged electrostatics in molecular simulations of macromolecular and ionic systems, the study of enzymatic reactions using hybrid QM/MM methods routinely employ truncation schemes for electrostatic interactions. The neglect of long-range interactions can lead to significant errors in the free energy profiles obtained from activated dynamics simulations.

In the present work, a new variational electrostatic projection (VEP) method is introduced that efficiently accounts for these long-range forces. The VEP method is used as the basis of a new Green’s function macromolecular solvent boundary potential (GFMSBP) for QM/MM calculations. Results are presented for several model ribozyme systems important to the study of RNA catalysis: the hammerhead ribozyme and the hairpin ribozyme. Results of QM/MM calculations on transphosphorylation thio effects that have implications into the interpretation of the kinetics of chemically modified ribozymes are also presented.
This work is supported by the Minnesota Supercomputing Institute (MSI) and the Army High Performance Computing Research Center (AHPCRC) under the auspices of the Department of the Army, Army Research Laboratory (ARL) under Cooperative Agreement number DAAD19-01-2-0014.

**Poster C8**

**John A. Keith**, Jonas Oxgaard, and William A. Goddard, III*
California Institute of Technology

**The Mechanism of Olefin Oxidation by Pd(II) Chloride Confirming the Mechanistic Chloride Dependence in the Wacker Process**

We carried out a mechanistic study of each step involved in the aqueous Pd-catalyzed olefin oxidation process (the Wacker process), without the copper co-catalyst to the formation of Pd$^0$. These studies used density functional theory (DFT) methods including Poisson-Boltzmann continuum solvation (PBF) to predict the free energies of structures optimized in solution (including saddle points). Our results indicate that the rate-determining step under low [Cl-] conditions is hydroxypalladation (PdCl$_3$(C$_2$H$_4$) + H$_2$O $\rightarrow$ PdCl$_3$CH$_2$CH$_2$OH + H$^+$) through internal attack by water, $\Delta G^\circ = 21.9$ kcal/mol. The rate-determining step under high [Cl-] conditions is chloride dissociation after external attack by water, $\Delta G^\circ = 18.3$ kcal/mol. The switch in mechanisms is caused by the prerequisite dissociation of Cl- prior to internal attack, which is inhibited by increased [Cl-]. Our calculated $\Delta G^\text{low} = \Delta G^\circ_{\text{low}} - \Delta G^\circ_{\text{high}} = 3.6$ kcal/mol corresponds well to the estimated experimental value of $\sim 3$ kcal/mol. Post hydroxypalladation, the reaction proceeds through a series of isoenergetic rearrangements. The last step of the process, release of acetaldehyde coupled with reduction of Pd$^{II}$ $\rightarrow$ Pd$^0$, occurs through an unexpected mechanism, best described as a water-catalyzed reductive deprotonation, with a calculated $\Delta G^\circ = 16.8$ kcal/mol.

**Poster C9**

**John L. Lewin** and Christopher J. Cramer
University of Minnesota

**Rapid Quantum Mechanical Models for the Computational Estimation of C–H Bond Dissociation Energies as a Measure of Metabolic Stability**

Several relatively inexpensive levels of theory are surveyed together with alternative algorithmic methods for the estimation of C–H bond dissociation energies (BDEs), such energies being useful for the prediction of metabolic stability in drug-like molecules. In particular, bond stretching potentials of several C–H bonds are computed using the AM1, PM3, HF/MIDI!, and B3LYP/MIDI! levels of electronic structure theory, and selected points are fit to Morse and parabolic potentials. BDEs computed by an AM1 fit to the Morse function show the smallest mean unsigned error in prediction ($\pm 3–4$ kcal mol$^{-1}$) over 32 diverse C–H bonds. An alternative method for correlating the AM1 parabolic force constant from a two-point unrelaxed potential provides only a slightly decreased accuracy and is computationally particularly inexpensive. Both methods should prove to be useful for the rapid *in silico* screening of drug-like molecules for metabolic stability to C–H bond oxidizing enzymes.

**Poster C10**

**Yun Liu** and Darrin M. York
University of Minnesota

**Density-Functional Study of Transphosphorylation Thio Effects in Model RNA Systems in Solution**

The most prominent mechanism for cell signaling, energy conversion, and the synthesis and breakdown of nucleic acids involves the transfer of phosphoryl groups. One method to probe the non-enzymatic and enzymatic
mechanisms of phosphoryl transfer reactions is to introduce site-specific chemical modifications, such as thio-substitution at the key phosphoryl oxygen positions. A resulting change in the reaction rate is termed a “thio effect.” Density-functional calculations of transphosphorylation thio effects in model RNA systems in solution are presented. Single thio substitutions at all of the phosphoryl oxygen positions (2’, 3’, 5’, pro-R and pro-S) and a double thio substitution at the non-bridging positions were considered. Free energy profiles and primary and secondary kinetic isotope effects for each reaction were calculated in the dianionic and monoanionic/monoprotic states, corresponding to alkaline and non-alkaline solution conditions, respectively.

Poster C11

Benjamin J. Lynch, Yan Zhao, and Donald G. Truhlar
University of Minnesota

Multi-Coefficient Correlation Methods Using the 6-31B(d) Basis Set: The BMC-QCISD and BMC-CCSD Methods for Thermochemistry and Thermochemical Kinetics

Many methods based on linear combinations of energy components calculated with explicitly-correlated molecular orbital methods have shown to provide excellent ratios of accuracy to cost for the calculation of thermochemical properties. We have developed a new basis set named 6-31B(d) which is balanced to predict thermochemical properties very accurately when used in the new multi-coefficient correlation methods BMC-QCISD and BMC-CCSD. The mean unsigned error for BMC-CCSD for calculating atomization energies, barrier heights, ionization potentials, and electron affinities is 22% lower than G3SX(MP2) at an order of magnitude less in cost for gradient calculations. The 6-31B(d) basis is also shown to have better performance than 6-31G(d) for explicitly-correlated calculations as well as density functional theory.

Poster C12

Dan T. Major, Yan Zhao, Donald G. Truhlar, and Jiali Gao
University of Minnesota

Mechanism of the Carbocation Cyclization in Trichodiene Synthase

Trichodiene synthase (TDS) catalyses the cyclization of farnesyl diphosphate (FPP) to form trichodiene in the biosynthesis of antibiotics and mycotoxins. The current work employs molecular dynamics (MD) simulation with a combined QM/MM Hamiltonian to study the function and molecular recognition of TDS. The TDS carbocation mechanism is elucidated by constructing a free energy profile for the multi-step reaction by utilizing one- and two-dimensional MD umbrella sampling simulations. The simulations reveal that the reaction proceeds via rapid sequential ring-closure and methyl migration steps, all with distinct intermediates. A hydride transfer step is likely to be a partially rate-limiting chemical step. Final deprotonation by the inorganic pyrophosphate or Asp100 is likely to trigger pyrophosphate and product release. Additionally, the conformational properties of the enzyme bound substrate, FPP, as well as that of the proposed intermediate, neurolidyl diphosphate (NPP), are studied. The MD simulations reveal that only NPP is folded correctly to initiate the cascade of carbocation reactions, thus supporting the notion that NPP is an obligatory intermediate.
Poster C13

Thomas Miller
University of Oxford

Torsional Path Integral Method for Predicting Biomolecular Conformation

The computational simulation of chemical and biological processes relies heavily on the ability of theoretical methods to accurately predict the preferred conformation of flexible molecules. Unfortunately, because of the large number of possible conformations and the subtle factors that determine their relative stability, this prediction is extremely challenging.

Standard theoretical methods for predicting molecular conformation generally make one of two assumptions. The first is the neglect of vibrational anharmonicity in the potential energy surface which can lead to failures in the description of conformational entropy and the effects of temperature on molecular conformation. Alternatively, when standard techniques do account for anharmonicity, they often neglect the important role of quantum mechanics in describing the light degrees of freedom, such as those involved in hydrogen bonding and solvation.

By applying the path integral Monte Carlo (PIMC) technique to the internal torsional motions of flexible molecules, we have developed the torsional PIMC technique for predicting molecular conformation. This new approach is efficient enough to apply to large molecules and accurate enough to quantitatively reproduce experimental results. Completed applications to a neurotransmitter molecule and to the glycine amino acid highlight the advantage of the method for cases in which anharmonicity and quantum effects are critical.

Most recently, the torsional PIMC technique has been extended to simulate the effects of explicit solvation on molecular conformation, and quantum dynamical calculations have been performed to explain a missing conformer of glycine.


Poster C14

Hisao Nakamura
University of Tokyo

First Principle Approach to Photochemical Reactions on Surfaces: Challenge to Reaction Dynamics of Substrate Excitation

Photochemical reactions on metal and semiconductor surfaces are one of developing area in surface science, and provide interesting problems connected with reaction dynamics including electronic excitation, charge transfer, relaxation, and nuclear dynamics. It is well known that adsorbate-surface interaction is local interaction and ab initio calculations provide very useful insights (e.g., new bond formation, static local charge transfer etc.) for ground states of systems. Because of locality of adsorbate-surface interaction, cluster or slab model is justified, and various ab initio methods can be applied. However, in surface photochemical reactions, many electronically excited states should be considered potentially with increasing of system size; thus it is unfeasible to apply highly developed post-HF methods such as CI. Furthermore excitation occurs indirectly in most photoreactions on surfaces, and an elementary process contains the following steps: (1) electron-hole pair creation in the substrate (bulk), (2) transport of these excitations to the surface region with relaxation, (3) attachment of hot electrons (holes) to adsorbate by tunneling, (4) promotion of nuclear dynamics (chemical reaction). As results, non-local electronic excitation and dynamic charge transfer must be considered.
In this presentation, we propose a theoretical model including the above electron dynamics and combine with a first principle DFT calculation scheme. Our model assumes that steps of optical excitation of substrate and of tunneling to an adsorbate are well separable. Electron-hole creation and transport are largely based on the framework of Berglund and Spicer [1], which was originally applied to photoemission processes, and many electron effects are mapped to effective one electron distribution function. For electron tunneling dynamics, we adopt non-equilibrium Green function (Keldysh) technique, which is rapidly developing in the field of molecular conductance/quantum transport problems. In both calculations, semi-infiniteness of substrate is estimated correctly within DFT level. The resulting method will be illustrated by photoinduced desorption of O$_2$ on Ag(110) surface, and photon energy dependence of reaction probability will be discussed.


**Poster C15**

**Robert W. Numrich** and Peter A. Rejto  
University of Minnesota

**An Extension of the Rutherford Formula**

The purpose of this talk is to extend the well known Rutherford formula for the scattering cross section, which is valid for the Coulomb potential. More specifically, first we introduce a class of central potentials which contains the Coulomb potential, both for positive and negative charges. Second, for completeness we show that for this class the scattering angle does exist. Third, we show that the scattering angle is a differentiable function of the impact parameter. We show this by showing that formal differentiation of the scattering angle leads to an improper integral whose finite part, in the sense of Hadamard, does exist. Furthermore, this derivative is given by this Hadamard finite part. Fourth, we show that for the Coulomb potential this Hadamard finite part formula implies the one of Rutherford. We hope to implement our work with a numerical algorithm to calculate this Hadamard finite part. In other words, we hope to calculate cross sections for our class of potentials.

**Poster C16**

**James A. Phillips**  
University of Wisconsin

**Condensed Phase Effects on Structure, Bonding, and Dynamics of CH$_3$CN–BF$_3$ and Related Complexes**

Complexes formed from nitrile donors and boron trifluoride have drawn much interest because their gas phase structures suggest partially formed B-N dative bonds, and furthermore, their structures change dramatically upon crystallization. The focus of this work has been to examine a series of related complexes not only to identify gas-solid structure differences, but also determine how these species respond to bulk, condensed-phase media, especially poorly-solvating environments such as inert gas matrices. As such, we employ a combination of computations, matrix isolation IR spectroscopy, and crystallography to probe structural changes that occur from medium-to-medium. We have obtained IR spectra of CH$_3$CN–BF$_3$ in solid argon and solid nitrogen, and have also conducted an extensive series of computations. Together, these data show clearly that these inert environments induce significant structural changes, including a substantial shortening of the B-N bond. Computations have also revealed that the B-N distance potential in CH$_3$CN–BF$_3$ is remarkably flat as a result of two nearly iso-energetic equilibrium structures. The dynamical implication is that large amplitude vibrational motion causes a genuine difference in the experimental (vibrationally-averaged) and theoretical (equilibrium) structures of the complex. This work has also been extended to complexes formed from other nitrile donors as well. Structural data have been obtained from both computations and x-ray crystallography, and IR spectra have been recorded in argon and nitrogen matrices, and also for the pure solid complexes. In general, crystal structures and/or solid state IR spectra indicate that all complexes examined have very similar structures in the solid state, with B-N distances of about
1.65 Å. Singly halogenated derivatives, e.g. F-CH₂CN–BF₃, are much more weakly bonded in the gas phase, and have B-N distances near 2.4 Å.

**Poster C17**

**Kevin Range¹, Evelyn Mayaan¹, L. J. Maher, III², and Darrin M. York¹**

¹University of Minnesota
²Mayo Clinic College of Medicine

**Electrostatics and DNA Bending: A COSMO and Monte-Carlo Study**

DNA bending is important for the packaging of genetic material, regulation of gene expression, and interaction with proteins. Consequently, it is of considerable interest to quantify the energetic factors required to induce bending of DNA such as base stacking and phosphate-phosphate repulsions. In the present work, the electrostatic contribution of phosphate-phosphate repulsions to the free energy of bending DNA is examined based on the crystallographic structure of DNA in a nucleosome core particle. A Green’s function approach based on a linear-scaling smooth conductor-like screening model is used to ascertain the contribution of individual phosphate-phosphate repulsions and overall electrostatic stabilization. The effect of charge neutralization by site-bound ions is considered using Monte Carlo simulation to characterize the distribution of ion occupations and free energy of bending as a function of counterion load. The calculations predict that the phosphate-phosphate repulsions account for approximately 30 percent of the total free energy required to bend DNA from the canonical linear B-form into the conformation found in the nucleosome core particle.

**Poster C18**

**Shingo Suzuki and Koichi Yamashita**
The University of Tokyo

**Optimal Control of Molecular Vibrational Wavepackets: Toward Quantum Computing**

Recently it has been proposed to use vibrational excitations in polyatomic molecules to encode qubits [1]. Each of the normal modes can be chosen to represent a qubit, and fundamental quantum logic operations, such as CNOT and Hadamard transformations, on qubits are performed by laser pulses which are designed with the help of optimal control theory (OCT). In our study, we investigate use of alternative vibrational modes of ammonia molecules as qubits. It is well known that the ammonia molecule is a two-level system and there are two eigenstates, |0⟩ₓ = (|u⟩ + |d⟩)/√2 and |1⟩ₓ = (|u⟩ − |d⟩)/√2, where |u⟩ corresponds to the eigenstate of the nitrogen above and |d⟩ to the one below the plane of the three hydrogens. Using these eigenstates as a qubit, Ferguson et al. proposed a scheme to attain a multi-qubit system by confining individual ammonia molecules inside fullerenes [2]. We construct a two-qubit system by adding the asymmetric vibrational ground and excited states |0⟩ₐ and |1⟩ₐ, to the two bending states. OCT is a very powerful tool for finding laser pulses ε(t) to promote an initial state ψᵢ(t = 0) = ϕᵢ into a target state ψᵣ(t = T) = ϕᵣ [3]. In view of the energy conservation of the laser field, the objective functional for optimal control is represented as

\[
J = \left| \langle \psi(T)|\phi_f \rangle \right|^2 - \alpha_0 \int_0^T \frac{|\epsilon(t)|^2}{s(t)} \, dt - 2\text{Re} \left[ \langle \psi(T)|\phi_f \rangle \int_0^T \langle \psi_f(t)| \frac{\partial}{\partial t} + i[H_0 + V + \mu \epsilon(t)]|\psi_i(t) \rangle \, dt \right].
\]
The optimal laser pulse for the Hadamard transformation, $|0\rangle_d |0\rangle_s \rightarrow (|0\rangle_d + |1\rangle_d) |0\rangle_s / \sqrt{2}$, was successfully obtained, and the time evolution of the vibrational wavepacket of the final entangled state was carefully investigated with focus on the decoherence of qubits (see Figure 1). Detailed analyses of our theoretical work will be discussed in the poster session.

Figure 1: Time evolution of vibrational wavepackets for $|0\rangle_d |0\rangle_s \rightarrow |0\rangle_d |0\rangle_s + |1\rangle_d |0\rangle_s$ and the optimal laser pulse.


Poster C19

Liqiang Wei, Michael J. Jamieson, and Alexander Dalgarno
Harvard University

Theoretical Study of Quantum Scattering Processes for Diatomic Hydrogen ($^2S$) and Oxygen ($^3P$) Complex

We present a quantum mechanical study of the diatomic hydrogen H($^2S$) and oxygen O($^3P$) collision and energy transfer for its four molecular symmetry ($X^2\Pi$, $^2\Sigma^+$, $^4\Sigma^-$), which is important for the investigation of many processes of astrophysical and chemical interests including the one on molecular cooling, trapping or Bose-Einstein condensation. We compute the rovibrational spectra for the ($X^2\Pi$) state and the resulting bound states are in an excellent agreement with experimental data for the energy range lower than the dissociation threshold. We calculate the phase shifts of its partial-waves, the total cross section, and the differential cross section. They are all well-structured because of the shape of its potential curve. We do the similar studies for the other three dissociative states ($^2\Sigma^+$, $^4\Pi$, $^4\Sigma^-$). Finally, we have also decided the thermal rate coefficients for the hydrogen and oxygen collision for its four individual states.

(arXiv: physics/0404145)

Poster C20

Scott Yockel, Benjamin Mintz, Xuelin (Nick) Wang, Pankaj Sinha, and Angela K. Wilson
University of North Texas

High Accuracy Molecular Properties: Successes and Challenges

The description of molecular properties to chemical accuracy has been a long-standing, but yet quite challenging, goal of computational chemistry. We examine difficulties and our recent strides toward achieving this goal, particularly from a basis set perspective. Our focus in this presentation is upon energetic, structural, and spectroscopic properties of a number of species ranging from first-row through transition metal species.
**Poster C21**

Chaoyuan Zhu, Shikha Nangia, Ahren W. Jasper, and Donald G. Truhlar  
University of Minnesota

*Coherent Switching With Decay of Mixing for Non-Born-Oppenheimer Trajectories*

We have developed the new semiclassical method, called coherent switching with decay of mixing (CSDM), in which the non-Born-Oppenheimer trajectories evolve continuously on a semiclassical Ehrenfest like potential energy surface and end on a pure electronic state eventually. This is accomplished by including decay of mixing terms in the evolution of electronic density matrix, and these decay terms generate a decoherent force that makes decay of mixing trajectories decohere gradually from Ehrenfest trajectories. We employ Tully’s fewest switches probability to take into account nonadiabatic transitions from one decoherent state to another and we treat each complete passage through a strong interaction region coherently. We carry out numerical tests using full dimensional tri-atomic two-sate model systems, where we compare exact quantum mechanical results with trajectory surface hopping, Ehrenfest, and other switching methods with decay of mixing. We find that the CSDM method is the most accurate of the methods tested.

**Poster C22**

Bethany L. Kormos, David L. Beveridge,* and Anne M. Baranger*  
Wesleyan University, Middletown, CT

*A Structural Investigation of U1A-RNA Mutants Using Molecular Dynamics*

Protein-RNA complexes are involved in all steps of mRNA processing. As such, knowledge of the process by which proteins are able to recognize and bind specific RNAs is critical for a complete understanding of the posttranscriptional regulation of gene expression. In almost all protein-RNA complexes studied to date, significant conformational changes in the protein, RNA or both have been observed, indicating that structural adaptation is an important aspect of the recognition process. However, structural adaptation is difficult to isolate and examine experimentally because it is but one of a number of phenomena that contribute to binding affinity and specificity of protein-RNA recognition. Molecular dynamics (MD) simulations are thus an ideal complement to experimental studies for the investigation of such structural adaptations, and can contribute to a better understanding of the protein-RNA recognition process.

The focus of this study is a particularly well-characterized system, the complex formed between the N-terminal domain of the protein U1A and stem loop 2 of U1 snRNA. Recognition of single-stranded RNA by U1A occurs through a structural motif called the RNA recognition motif (RRM), also known as the ribonucleoprotein (RNP) domain or the RNA binding domain (RBD). The RRM consists of a $\beta_1\alpha_1\beta_2\alpha_2$ fold, which forms a four-stranded antiparallel $\beta$-sheet supported by two $\alpha$-helices. The N-terminal RRM of U1A contains two out of three highly conserved aromatic amino acids that are found on the surface of the $\beta$-sheet and are known to stack with RNA bases upon binding. Baranger and co-workers have found that mutation of one of these highly conserved residues, Phe56, can lead to up to a 5.5 kcal mol$^{-1}$ destabilization of the complex.

In this study, MD is used to explore the structural role of Phe56 in the U1A-RNA recognition process. Specifically, simulations of U1A and stem loop 2 RNA have been performed in both free and bound states for wild-type and Phe56Ala, Phe56Leu and Phe56Trp mutants. Structural analyses of these simulations are done not only to contribute to an understanding of the loss in binding energy seen experimentally, but with the intent of probing the greater issue of structural adaptation. To this end, the analysis
presented involves the investigation of both local and global structural changes in protein and RNA associated with the mutation of Phe56.

**Poster C23**

**Orlando Roberto-Neto**¹, Fernando R. Ornellas², and Francisco B. C. Machado³

¹Instituto de Estudos Avançados, Centro Técnico Aeroespacial
²Universidade de São Paulo
³Instituto Tecnológico de Aeronáutica, Centro Técnico Aeroespacial

**Dual-Level Direct Dynamics Calculations of the Kinetic Isotope Effects for the CH₄ + F → CH₃ + HF Abstraction Reaction**

Kinetic isotope effects (KIEs) for hydrogen abstraction from the isotopomers CH₄, ¹³CH₄, and CD₄ by fluorine atoms have been studied by the variational transition state theory with multidimensional tunneling contributions (VTST/MT). Low-level calculations of the potential surface were carried out within the AM1-SRP approach. High-level structural and energetic properties of the reactants, transition state, and products were obtained with the MP2 and CCSD(T) theories and the cc-pVQZ basis set, and were used to interpolate corrections to the low-level calculations. The values of the classical barrier height (ΔVₚ) and the energy of reaction (ΔE), which are employed as high-level energetic parameters, are set equal to 1.8 kcal/mol and 28.5 kcal/mol, respectively. The chemical dynamics results show that large-curvature tunneling (LCT) paths provide the dominant contribution, with significant participation of excited vibrational states. At the CVT/µOMT level, the calculated value of H/D KIE is equal to 1.74 at 298 K, which is in very close agreement with experiment (1.4—1.7). The ¹²C/¹³C KIE is calculated to have a very small variation in the temperature range of 200 to 2000 K. CVT/µOMT activation energies at the temperature ranges of 200—300 K and 200—400 K are equal to 0.59 and 0.73 kcal/mol, respectively, which are comparable to the experimental values of 0.43 and 0.53 kcal/mol.
**Poster C24**

**Becky L. Eggimann**, Gianluigi Veglia, and J. Ilja Siepmann  
University of Minnesota

*Protein structure prediction using minimal NMR data and a simple residue-based force field*

Knowledge of three-dimensional structure is an essential step in the process of defining the biological role of a protein. While experimental techniques, such as X-ray crystallography and NMR spectroscopy, are capable of determining high-resolution protein structures (» 1 Å RMSD), the increasing number of protein sequences becoming available demands that more efficient methods for generating structural models be found. Structure prediction algorithms have been designed to generate three-dimensional structural models of proteins based solely on sequence information, and provide a comparatively quick assessment of global folds. However, the gain in speed is offset by a loss in accuracy of the determined structures. Even the best de novo prediction algorithms generate correct overall topology in roughly 50% of their attempts, while typical RMSDs fall in the 4-8 Å range. A promising alternative is the use of a combined experimental and computational approach to structure prediction where the strengths of both techniques can be emphasized. We present a Monte Carlo simulated annealing method using a simple, residue-based potential function supplemented with experimental constraints obtained from NMR spectroscopy. Due to recent advances in sample preparation techniques, measurement of both distances and orientational constraints from solution NMR experiments has become routine. The combination of a force field, orientational constraints, and distance constraints yields protein structures with improved accuracy over each method alone, while still relying on minimal experimental input. Results for a set of six multi-helical proteins will be shown.

**Poster C25**

**Ling Zhang** and J. Ilja Siepmann  
University of Minnesota

*Pressure Dependence of the Vapor-liquid-liquid Phase Behavior of Ternary Mixtures of n-alkanes, n-perfluoroalkanes and Carbon Dioxide*

Expansion of an organic solvent by an inert gas can be used to tune the solvent's liquid density, solubility strength and transport properties. In particular, gas expansion can be used to induce miscibility at low temperatures for systems that are biphasic at standard pressure. Con gurational-bias Monte Carlo simulations in the Gibbs ensemble using the transferable potential for phase equilibria force field were carried out to investigate the liquid|liquid|vapor equilibria and the microscopic structures for two ternary systems: n-decane/n-perfluorohexane/carbon dioxide and n-hexane/n-perfluorodecane/carbon dioxide. The calculated upper critical miscibility pressures at 298 K are in satisfactory agreement with the available experimental data. The simulations yield strongly asymmetric compositions for the coexisting liquid phases and different degrees of microheterogeneity as measured by local composition enhancements.
## Index of Authors

*Bold* typeface denotes poster presenter.

<table>
<thead>
<tr>
<th>Author</th>
<th>Index</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albu, Titus V.</td>
<td></td>
<td>A22(i), A22(ii)</td>
</tr>
<tr>
<td>Allison, Thomas C.</td>
<td></td>
<td>A25</td>
</tr>
<tr>
<td>Anderson, Amos</td>
<td></td>
<td>A1</td>
</tr>
<tr>
<td>Alexander, M. H.</td>
<td></td>
<td>C3(i)</td>
</tr>
<tr>
<td>Aoiz, F. J.</td>
<td></td>
<td>C3(ii)</td>
</tr>
<tr>
<td>Bacelo, Daniel E.</td>
<td></td>
<td>B2</td>
</tr>
<tr>
<td><strong>Bachrach, Steven M.</strong></td>
<td></td>
<td>B1</td>
</tr>
<tr>
<td>Balasubramanian, Krishnan</td>
<td></td>
<td>A14(ii)</td>
</tr>
<tr>
<td>Balucani, N.</td>
<td></td>
<td>C3(i), C3(ii)</td>
</tr>
<tr>
<td>Bañares, L.</td>
<td></td>
<td>C3(ii)</td>
</tr>
<tr>
<td>Baranger, Anne M.</td>
<td></td>
<td>C22</td>
</tr>
<tr>
<td>Basak, Subhash C.</td>
<td></td>
<td>A14(i), A14(ii), A15</td>
</tr>
<tr>
<td>Baxter, Eric</td>
<td></td>
<td>C2</td>
</tr>
<tr>
<td>Belytschko, Ted</td>
<td></td>
<td>B13</td>
</tr>
<tr>
<td>Beveridge, David L.</td>
<td></td>
<td>C22</td>
</tr>
<tr>
<td><strong>Bhatt, Divesh</strong></td>
<td></td>
<td>C1</td>
</tr>
<tr>
<td>Bhattacharyay, Sudeep</td>
<td></td>
<td>A2</td>
</tr>
<tr>
<td><em>Binning, Jr., R. C.</em></td>
<td></td>
<td>B2</td>
</tr>
<tr>
<td>Blanco, Mario</td>
<td></td>
<td>A1</td>
</tr>
<tr>
<td>Bobbenkamp, R.</td>
<td></td>
<td>C3(ii)</td>
</tr>
<tr>
<td><strong>Boudreaux, Edward A.</strong></td>
<td></td>
<td>C2</td>
</tr>
<tr>
<td><strong>Brandão, J.</strong></td>
<td></td>
<td>B22, B24</td>
</tr>
<tr>
<td>Brooks, III, Charles L.</td>
<td></td>
<td>B26</td>
</tr>
<tr>
<td>Bussery-Honvaut, B.</td>
<td></td>
<td>C3(ii)</td>
</tr>
<tr>
<td>Callis, Patrik R.</td>
<td></td>
<td>B10</td>
</tr>
<tr>
<td>Capecchi, G.</td>
<td></td>
<td>C3(i)</td>
</tr>
<tr>
<td>Capozza, G.</td>
<td></td>
<td>C3(i), C3(ii)</td>
</tr>
<tr>
<td>Cartechini, L.</td>
<td></td>
<td>C3(ii)</td>
</tr>
<tr>
<td><strong>Casavecchia, P.</strong></td>
<td></td>
<td>C3(i), C3(ii)</td>
</tr>
<tr>
<td>Cervantes, Albert</td>
<td></td>
<td>A1</td>
</tr>
<tr>
<td>Chakraborty, Arindam</td>
<td></td>
<td>A3</td>
</tr>
<tr>
<td>Chuang, Yao-Yuan</td>
<td></td>
<td>B3</td>
</tr>
<tr>
<td>Corelli, S. A.</td>
<td></td>
<td>A4</td>
</tr>
<tr>
<td>Corchado, J.C.</td>
<td></td>
<td>B5</td>
</tr>
<tr>
<td>Cramer, Christopher J.</td>
<td></td>
<td>A24, C6, C9</td>
</tr>
<tr>
<td><strong>Cruz Hernández, Norge</strong></td>
<td></td>
<td>B4</td>
</tr>
<tr>
<td>Cullen, John</td>
<td></td>
<td>C4</td>
</tr>
<tr>
<td>Dalgarno, Alexander</td>
<td></td>
<td>C19</td>
</tr>
<tr>
<td>da Silva, B. C. N.</td>
<td></td>
<td>B24</td>
</tr>
<tr>
<td><strong>Dudley, Timothy J.</strong></td>
<td></td>
<td>A26</td>
</tr>
<tr>
<td>Eggimann, Becky L.</td>
<td></td>
<td>C24</td>
</tr>
<tr>
<td>Elkner, Kenneth</td>
<td></td>
<td>B2</td>
</tr>
<tr>
<td>Ellingson, Benjamin A.</td>
<td></td>
<td>A5</td>
</tr>
<tr>
<td>El-Masri, Hisham</td>
<td></td>
<td>A14(i)</td>
</tr>
<tr>
<td><strong>Espinosa-García, J.</strong></td>
<td></td>
<td>B5</td>
</tr>
<tr>
<td>Ferrer, S.</td>
<td></td>
<td>A18</td>
</tr>
<tr>
<td>Fisher, Daniel</td>
<td></td>
<td>A1</td>
</tr>
<tr>
<td>Name</td>
<td>Page(s)</td>
<td></td>
</tr>
<tr>
<td>-------------------------------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>Freedman, Holly</td>
<td>C5</td>
<td></td>
</tr>
<tr>
<td>French, Alfred D.</td>
<td>A6</td>
<td></td>
</tr>
<tr>
<td>Gao, Jiali</td>
<td>A2, B12, C12, B14, A17</td>
<td></td>
</tr>
<tr>
<td>García-Cruz, I.</td>
<td>B6</td>
<td></td>
</tr>
<tr>
<td>Gherman, Benjamin F.</td>
<td>C6</td>
<td></td>
</tr>
<tr>
<td>Giese, Timothy J.</td>
<td>A7</td>
<td></td>
</tr>
<tr>
<td>Giesen, Dave</td>
<td>B7</td>
<td></td>
</tr>
<tr>
<td>Glaser, Rainer</td>
<td>B20</td>
<td></td>
</tr>
<tr>
<td>Goddard III, William A.</td>
<td>A1, C8</td>
<td></td>
</tr>
<tr>
<td>González, Carlos A.</td>
<td>A25</td>
<td></td>
</tr>
<tr>
<td>González, Ines</td>
<td>A25</td>
<td></td>
</tr>
<tr>
<td>Gordon, Mark S.</td>
<td>A26</td>
<td></td>
</tr>
<tr>
<td>Gregersen, Brent A.</td>
<td>C7</td>
<td></td>
</tr>
<tr>
<td>Hagedorn, George A.</td>
<td>A8</td>
<td></td>
</tr>
<tr>
<td>Haug, Kenneth</td>
<td>B8</td>
<td></td>
</tr>
<tr>
<td>Hawkins, Douglas M.</td>
<td>A14(i)</td>
<td></td>
</tr>
<tr>
<td>Honvault, P.</td>
<td>C3(ii)</td>
<td></td>
</tr>
<tr>
<td>Jamieson, Michael J.</td>
<td>C19</td>
<td></td>
</tr>
<tr>
<td>Jasper, Ahren W.</td>
<td>B23, C21</td>
<td></td>
</tr>
<tr>
<td>Karaboni, Sami</td>
<td>A21</td>
<td></td>
</tr>
<tr>
<td>Keith, John A.</td>
<td>C8</td>
<td></td>
</tr>
<tr>
<td>Khandogin, Jana</td>
<td>B26</td>
<td></td>
</tr>
<tr>
<td>Kim, Kyung Hyun</td>
<td>B9(i), B9(ii), B9(iii)</td>
<td></td>
</tr>
<tr>
<td>Kim, Seon Ho</td>
<td>A9</td>
<td></td>
</tr>
<tr>
<td>Kim, Yongho</td>
<td>A9, B9(i), B9(ii), B9(iii)</td>
<td></td>
</tr>
<tr>
<td>Klotz, Wendy L.</td>
<td>B25</td>
<td></td>
</tr>
<tr>
<td>Knapp, Ernst-Walter</td>
<td>B18</td>
<td></td>
</tr>
<tr>
<td>Kormos, Bethany</td>
<td>C22</td>
<td></td>
</tr>
<tr>
<td>Kowalski, Karol</td>
<td>A11</td>
<td></td>
</tr>
<tr>
<td>Krimm, Samuel</td>
<td>A16</td>
<td></td>
</tr>
<tr>
<td>Kungwan, N.</td>
<td>A23</td>
<td></td>
</tr>
<tr>
<td>Launay, J.-M.</td>
<td>C3(ii)</td>
<td></td>
</tr>
<tr>
<td>Lawrence, C. P.</td>
<td>A4</td>
<td></td>
</tr>
<tr>
<td>Lewin, John L.</td>
<td>C9</td>
<td></td>
</tr>
<tr>
<td>Lim, Ed</td>
<td>A25</td>
<td></td>
</tr>
<tr>
<td>Lin, Hai</td>
<td>A10</td>
<td></td>
</tr>
<tr>
<td>Lin, Myat</td>
<td>B8</td>
<td></td>
</tr>
<tr>
<td>Liu, Tiqing</td>
<td>B10</td>
<td></td>
</tr>
<tr>
<td>Liu, Yun</td>
<td>C10</td>
<td></td>
</tr>
<tr>
<td>Lodriguito, Maricris D.</td>
<td>A11</td>
<td></td>
</tr>
<tr>
<td>Lonergan, Nathaniel J.</td>
<td>B8</td>
<td></td>
</tr>
<tr>
<td>López, Carlos Silva</td>
<td>B11, B15</td>
<td></td>
</tr>
<tr>
<td>Lynch, Benjamin J.</td>
<td>C11, B21</td>
<td></td>
</tr>
<tr>
<td>Lynch, Vanessa Audette</td>
<td>A12</td>
<td></td>
</tr>
<tr>
<td>Ma, Shuhua</td>
<td>B12</td>
<td></td>
</tr>
<tr>
<td>Machado, Francisco B. C.</td>
<td>C23</td>
<td></td>
</tr>
<tr>
<td>Maher, III, L. J.</td>
<td>C17</td>
<td></td>
</tr>
<tr>
<td>Major, Dan T.</td>
<td>C12</td>
<td></td>
</tr>
<tr>
<td>Martí, S.</td>
<td>A18</td>
<td></td>
</tr>
<tr>
<td>Martínez-Magadán, J. M.</td>
<td>B6</td>
<td></td>
</tr>
<tr>
<td>Mayaan, Evelyn</td>
<td>C17</td>
<td></td>
</tr>
<tr>
<td>McGrath, Matthew J.</td>
<td>A13</td>
<td></td>
</tr>
</tbody>
</table>

42
Mielke, Steven L.  A12
Mielke, Steven L.  B13
Mikel, Sean E.  A22(i), A22(ii)
Miller, Thomas  C13
Mills, Denise  A14(i), A14(ii), A15
Mintz, Benjamin  C20
Mogo, C. F. N. F.  B24
Moliner, V.  A18
Mumtaz, Moiz M.  A14(ii)
Nakamura, Hisao  C14
Nam, Kwangho  B14
Nangia, Shikha  B23, C21
Natarajan, Ramanathan  A15
Navarrete, M.  B5
Nieto Faza, Olalla  B11, B15
Numrich, Robert W.  C15
Ornellas, Fernando R.  C23
Oxgaard, Jonas  C8
Palmo, Kim  A16
Pang, Yuan-Ping  B16
Phillips, James A.  C16
Piecuch, Piotr  A11
Pu, Jingzhi  A17
Rai, Neeraj  B17
Range, Kevin  C17
Rangel, C.  B5
Rejto, Peter A.  C15
Rio, Carolina M. A.  B22
Roberto-Neto, Orlando  C23
Rodriguez de Lera, Angel  B11, B15
Rosa, Carla J.  B24
Ruiz-Pernía, J. J.  A18
Sanz, Javier Fdez.  B4
Scanlon, Joseph D.  A24
Schatz, George C.  B13
Schmidt am Busch, Marcel  B18
Schmidt, J. R.  A4
Schroder, Peter  A1
Schure, Mark R.  B25
Segoloni, E.  C3(i), C3(ii)
Siepmann, J. Ilja  C1, B17, B25, A21, C24, C25
Sinha, Pankaj  C20
Skinner, J. L.  A4
Skouteris, D.  C3(i)
Stankovich, Marian T.  A2
Sun, Li  B25
Suzuki, Shingo  C18
Takayanagi, Toshiyuki  A19
Tolman, William B.  C6
Troya, Diego  B13
Truhlar, Donald G.  A3, A5, A10, B23, C11, A12, C12, A17, B21, C21
Truong, Thanh N.  A23, C5