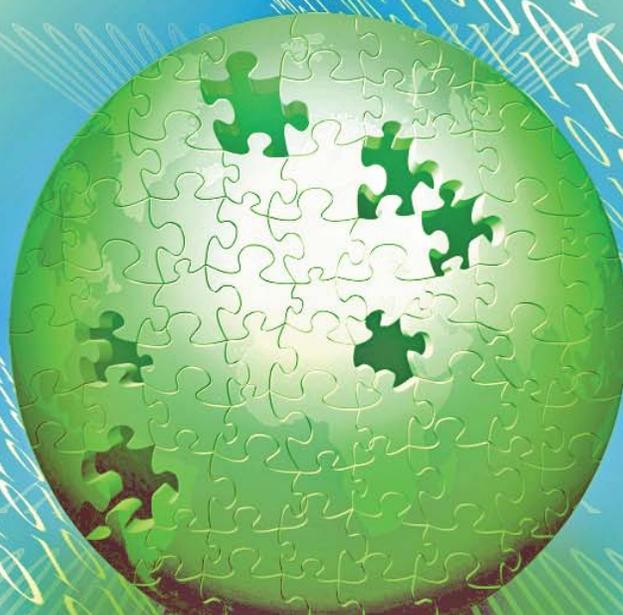


11th Annual CERMM Symposium

June 4 - 5, 2011

Concordia University, Montréal



Centre for Research in Molecular Modeling

CERMM

Centre de recherche en modélisation moléculaire



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Symposium Program

Saturday, June 4, 2011. Richard J. Renaud Science Complex, SP-S110

9:45 Welcoming remarks

Gilles Peslherbe, Director, Centre for Research in Molecular Modeling

Discussion Leader: **Gilles Peslherbe**

9:50 John Tromp (Vanier College)

A New Course in Spectroscopy at Vanier College

10:10 Osama Ali and Travis Fridgen (Memorial University)

Structures of M^{2+} /Uracil Complexes by Collision Induced Dissociation CID and IRMPD Spectroscopy in the N-H/O-H Stretching Region

10:30 Yaoting Zhang and Cory Pye (St-Mary's University)

Ab Initio Study of Low pH Vanadium (V) Species

10:50 Peter Boyd, Tom Daff, David van Rijswijk and Tom Woo (University of Ottawa)

Advances in the Molecular Modeling of Metal Organic Frameworks for Carbon Dioxide Capture

11:10 Coffee Break

Discussion Leader: **Pierre-Nicolas Roy**

11:30 Barbara Goodall, E. Walker and Cory Pye (St-Mary's University)

Ab initio Study of Hydrated HVO_4^{2-}

11:50 Stephen Constable and Pierre-Nicholas Roy (University of Waterloo)

Accelerated Molecular Dynamics in the Molecular Modelling Tool Kit using Graphical Processing Units

12:10 Ivan Saika-Voivod (Memorial University of Newfoundland), Louis Poon (University of Saskatchewan) and **Richard Bowles** (University of Saskatchewan)

The Role of FCC Tetrahedral Subunits in the Phase Behavior of Medium-sized Lennard-Jones Clusters

12:30 Lunch

Discussion Leader: **Tony Whitehead**

- 13:30 Keynote Lecture: Piotr Piecuch** (Michigan State University)
Local Correlation Coupled-Cluster Methods Exploiting Cluster-In-Molecule Ansatz and Their Multi-Level Extensions
- 14:30 Tao Zeng**, Hui Li, Robert Le Roy, and Pierre-Nicholas Roy (University of Waterloo)
The Nature of Molecular Hydrogen under Nano-Confinement: Insight from Theory and Simulations
- 14:50 Christopher Ing** and Pierre-Nicholas Roy (University of Waterloo)
Applications of Ring-Polymer Molecular Dynamics and Path Integral Ground State Methods to He-CO₂ and Biomolecules
- 15:10 Jing Yang**, Christopher Ing and Pierre-Nicholas Roy (University of Waterloo)
Effective Potential Approach to the Simulation of Large Para-hydrogen Clusters and Droplets
- 15:30 Coffee Break**

Discussion Leader: **Pradeep Varadwaj**

- 15:50 Hui Li**, Robert J. Le Roy, and Pierre-Nicholas Roy (University of Waterloo)
Superfluidity in Mixed Helium-Hydrogen Quantum Solutions Doped with a Chromophore Molecules
- 16:10 Alya Arabi** (Dalhousie University) and Chérif Matta (Dalhousie University and Mount Saint Vincent University)
Electric Field-Effects on Proton Transfer Kinetics in Formic Acid Dimer
- 16:30 Soran Jahangiri** (Concordia University), Grygoriy Dolgonos (University of Bremen), Thomas Frauenheim (University of Bremen) and Gilles Peslherbe (Concordia University)
Investigation of Ionic Cluster Hydration with the Newly Parameterized Self-Consistent Charge Density-Functional Tight Binding Model
- 16:50 Sima Mehrpajouh**, Gilles Peslherbe and Heidi Muchall (Concordia University)
A Computational Investigation of Nitrilimine Cycloaddition Reactions
- 17 :10 Louis-Philippe Simoneau** and Alain Rochefort (Ecole Polytechnique de Montréal)
Modeling of Percolation in Size Distributed Carbon Nanostructures Networks

17 :30 Arnaud Maillard and Alain Rochefort (Ecole Polytechnique de Montréal)
Band Alignment Optimization of rrP3HT/C₆₀ Bulk Heterojunction

18:00 Poster Session and Reception sponsored by Azuris Technologies Inc.

Sunday, June 5, 2011. J.A deSeve Cinema, LB-125.

Discussion Leader: **Richard Bowles**

10:00 Thomas Morgan, Theo van de Ven and **Tony Whitehead** (McGill University)
Determining the Structure of Dialdehyde Functionalized Cellulose Nanocrystals using Semi-Empirical Molecular Modelling

10:20 Kevin Conley, Theo van de Ven and Tony Whitehead (McGill University)
The Molecular Structure of Crystalline Cellulose using Ab-initio and PM6 Semi-Empirical Calculations

10:40 Corey MacDonald and Russell Boyd (Dalhousie University)
Catalytic Mechanism of FK506-Binding Protein 35 with Tacrolimus

11:00 Coffee Break

Discussion Leader: **Shihao Wang**

11:20 Sean Collins, **Gavin Heverly-Coulson**, and Russell Boyd (Dalhousie University)
Reaction of Group 16 Analogues of Ethoxyquin with Hydrogen Peroxide, a Computational Study

11:40 WenJuang Huang and James Gauld (University of Windsor)
Mechanism Study of FAD Catalyzed UDP -Galactopyranose Mutase Processes: QM/MM and DFT Investigations

12:00 Mohidus Samad Khan, Tony Whitehead and Theo van de Ven (McGill University)
Semi-empirical Molecular Modelling of Picloram specific Antibody

12:00 Lunch

13:30 Russell Boyd (Dalhousie)

A Brief History of Computational Chemistry in Canada

Poster Presentations

1. *Interaction of Poly-Peptides with Denaturants as a Possible Model to Investigate the Mechanism of Protein Denaturation*
Xijun Wang and Gilles Peslherbe (Concordia University)
2. *Trends in Hydrogen Bonding within the Solvation Shells of Amino Acids: An Ab Initio Molecular Dynamics Study*
Laura Albrecht and Russell Boyd (Dalhousie University)
3. *Heterogeneous Condensation of the Lennard-Jones Vapor Onto a Nanoscale Seed Particle*
Levent Inci and Richard Bowles (University of Saskatchewan)
4. *Using a Genetic Algorithm to Investigate the Structure of Samarium-Doped Ceria*
Arif Ismail, James Hooper, Javier Giorgi and Tom Woo (University of Ottawa)
5. *Ground-State Properties of LiH by Reptation Quantum Monte Carlo*
Egor Ospadov, Daniel Oblinsky and Stuart Rothstein (Brock University)
6. *Conformational Mobility in Cytochrome P450 from Piezophilic Bacteria Photobacterium Profundum SS9*
Liliya Shamova (Kazan Federal University), Anastasia Bakulina (State Research Center of Virology and Biotechnology Vector) and Elena Sineva (University of California San Diego)
7. *Exploration of Electronic Structure Based Descriptors for 3D QSAR Models of Asymmetric Catalysis*
Nicholas Trefiak and Tom Woo (University of Ottawa)
8. *Mapping Approach to Quantum-Classical Dynamics*
Ali Nassimi (University of Calgary)
9. *Theoretical Studies of Electron Solvation in Photoexcited Iodide-Solvent Clusters*
Chun Mak and Gilles Peslherbe (Concordia University)
10. *Computer Simulations of O₂ Diffusion in the Human Hemoglobin Tetramer*
Mariya Shadrina, Ann English and Gilles Peslherbe (Concordia University)
11. *Exploratory Computational Studies Towards the Photo-Induced Degradation of Lignin*
Lei Zhang, Gilles Peslherbe and Heidi Muchall (Concordia University)
12. *A New Basis for Computing Rovibrational Spectra of Polyatomic Molecules*
Xiao-Gang Wang and Tucker Carrington Jr. (Queen's University)
13. *Semi-Empirical Quantum Models for Chemical Reactions in Zinc Metalloenzymes*
Shihao Wang and Guillaume Lamoureux (Concordia University)

ABSTRACTS

Talks

A New Course in Spectroscopy at Vanier College

John Tromp
Vanier College

Vanier College will be offering a new option course for science students called Physical Chemistry in the fall of 2011. The course will focus on molecular spectroscopy, simple quantum mechanics, spectroscopic data analysis to extract molecular parameters using excel, and finite differences as a numerical calculation technique.

Students taking the course would have taken an introductory physics course on mechanics and an introductory math course of differential calculus as well as a general chemistry course where they have been exposed to the hydrogen atom spectrum and are familiar with $\lambda\nu=c$; $E=h\nu$; $E_n=-B/n^2$ for H and the Bohr idea of photons being absorbed or emitted in transitions between discrete energy levels.

In the new course, they will learn that molecules rotate and vibrate and review the classical mechanics both analytically and numerically for these types of motion. In molecules, these motions obey quantum mechanics, so that photons in the infrared region are emitted or absorbed in transitions between vibrational levels, while microwave photons are involved in rotational transitions. They will also see what sorts of molecular information can be extracted by different types of spectroscopy, for example bond lengths from microwave spectroscopy, and force constants and bond dissociations energies from vibrational spectroscopy.

This course was inspired by Chemistry 209, currently taught by R. J. LeRoy at the University of Waterloo, but will also include numerical techniques in excel similar to examples outlined in a presentation "Finite Differences: An approach that has no limits" by John Tromp at CERMM 2008. The goal is to deepen the students understanding of molecular motions both classically and quantum mechanically, giving them the pragmatic tool of finite differences as a general way to approach dynamics numerically.

***Structures of M^{2+} Uracil Complexes by Collision Induced Dissociation
CID and IRMPD Spectroscopy in the N-H/O-H Stretching Region***

Osama Ali and Travis Fridgen
Memorial University

Interactions between divalent metal ions and uracil have been investigated using mass spectrometry (FTICR) in combination with theoretical calculations. Positive ion electrosprayspectra show that $[M(\text{Ura})(\text{Ura-H})]^+$ (M=divalent metal ions) is the most abundant ion at low concentrations (mM). MS/MS experiments show that the lowest energy decomposition pathway for $[M(\text{Ura})(\text{Ura-H})]^+$ (M = Zn^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , Mn^{2+} , Cd^{2+} , Pd^{2+} , Mg^{2+} and Ca^{2+}) is not loss of uracil, but is loss of HNCN followed by HCN. This loss has been confirmed by using the isotope labeling of uracil. The potential energy surfaces associated with the elimination from $[\text{Cu}(\text{Ura})(\text{Ura-H})]^+$ are represented by various CID products. Under CID and even the even softer, IRMPD, conditions $[\text{Pb}(\text{Ura})(\text{Ura-H})]^+$ and $[\text{Ba}(\text{Ura})(\text{Ura-H})]^+$ behave very differently. These complexes dissociate by losing uracil directly. The computed binding energies between neutral uracil and $[M(\text{Ura-H})]^+$, M=Mg, Cu, Ca, Ba and Pb have been calculated. The differences in the uracil binding energies are consistent with the experimentally-observed differences in fragmentation pathways. Spectroscopic characterization is a common technique used to study structures in the gas phase and provides an optimal approach to determining a structure and supporting our CID experiments. Consequently, IRMPD spectroscopy experiments enable us to sort out the geometries of the dimer complexes. Complexes of uracil and lead metal ions, as well the water-solvated complexes have been investigated by infrared multiple photon dissociation (IRMPD) spectroscopy in the N-H and O-H stretching region $3200\text{-}3900\text{ cm}^{-1}$. Calculations were performed using B3LYP and the final energies were obtained at the MP2/6-311++G(2d,p) level of theory. The IRMPD spectra clearly show the N-H stretching, and the O-H stretching vibrations for the solvated ions. In all cases, the computed IR spectra for the lowest energy structures are consistent with the experimental IRMPD spectrum to clarify structures of each complex. The experimental spectra for $[\text{Pb}(\text{Ura-H})(\text{H}_2\text{O})_n]^+$ (n=1-2) revealed that the first water molecule binds to the lead ion and indicates the presence of intramolecular hydrogen bonding to a carbonyl of uracil. The second molecule of water also attaches directly to the lead ion, but does not participate in any hydrogen bonding.

Ab Initio Study of Low pH Vanadium (V) Species**Yaoting Zhang and Cory Pye**

Saint Mary's University

Chemical speciation of natural vanadium (V) is not fully known because of its complexity and low abundance. However, recent applications of vanadium (IV) and (V) in battery research and drug industry require the detailed structural information of the element [1,2]. Our research goal is to preliminary investigate hydration properties of VO_2^+ , H_3VO_4 and H_2VO_4^- in the gas phase. We used ab initio methods MP2 and B3LYP with 6-31G* and 6-31+G* methods to optimize geometries and produce vibrational frequencies. The hydration effect on bond lengths and vibrational frequencies were investigated. The mechanism of H_3VO_4 transformation to VO_2^+ in acidic conditions also have been studied and one intermediate have been identified.

[1] Thompson, K.H., Lichter, J., LeBel, C.L., Scaife, M.C, McNeill, J.H., Orvig, C. *J. Inorg. Biochem.* **2009**, *103*, 554.

[2] You, D., Zhang, H., Sun, C., Ma, X.. *J of Power Sources.* **2011**, *196*, 1578.

Advances in the Molecular Modeling of Metal Organic Frameworks for Carbon Dioxide Capture

Tom Daff, David van Rijswijk and Tom Woo
University of Ottawa

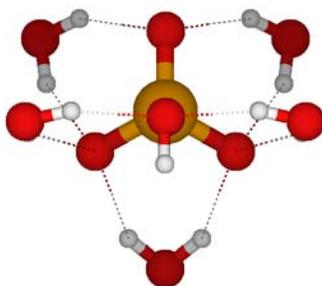
Metal organic frameworks (MOFs) are an emerging class of microporous materials which are generating considerable interest due to their exceptional ability to capture CO₂ for carbon dioxide sequestration and storage applications. The current challenge in this field is to produce materials which can selectively adsorb CO₂ over other combustion exhaust gases. With the aid of computational analysis, insight into the binding properties of existing MOFs has been obtained, however, this analysis has had limited application in a predictive capacity. There are a large number of challenges in applying molecular modeling to predicting novel MOFs for gas capture. Included in these challenges are the accuracy of the parameters used to describe gas uptake in each system, the accuracy of the level of theory used to predict new structures, and efficiently sampling the vast number of possible configurations of metals and organic linkers to generate proposed structures. In this presentation, our groups recent advances in simulating MOFs with the goal of both understanding current generation materials as well as aiding in the design of novel MOFs will be presented. These include our efforts to develop a high throughput screening approach to simulate the gas adsorption properties of MOFs and automated analysis tools to identify MOFs with desirable CO₂ capturing properties.

Ab initio Study of Hydrated HVO_4^{2-}

Barbara Goodall, V.E.J. Walker and Cory Pye
Saint Mary's University

The aquachemistry of toxic vanadium(V) is complex. Structural properties of hydrated HVO_4^{2-} is not fully understood because of its low concentration [1]. The calculations performed offer a prediction of the structure of HVO_4^{2-} that is likely to exist. The structures, energies and vibrational frequencies of $\text{HVO}_4^{2-}(\text{H}_2\text{O})_n$, $n=1-6$ have been calculated by Hartree-Fock (HF), second order Moller-Plesset (MP2) and B3LYP levels of theory. These frequencies and bond lengths are measurements that in theory should follow the same trend as experimental data collected from IR, Raman and solution X-ray or neutron diffraction.

[1] Richens, D. T. *The Chemistry of Aqua Ions*; Wiley: Chichester, **1997**; pp. 240-243.



***Accelerated Molecular Dynamics in the Molecular Modelling Tool Kit
using Graphical Processing Units***

Stephen Constable and Pierre-Nicholas Roy
University of Waterloo

Molecular Dynamics (MD) is a computational tool that allows for microscopic investigation of chemical systems, including the prediction of free energy changes and reaction rate constants. It has been found that using Graphical Processing Units (GPUs) for MD offers orders of magnitude increases in computational power versus traditional Central Processing Units (CPUs). This allows for longer, more accurate simulations especially for the large system size inherent in the life sciences. The Molecular Modelling Tool Kit (MMTK) software is used to perform MD simulations, and can be augmented to take advantage of a GPU MD code. This will provide increased computational efficiency to software users. Programming of the GPU will be achieved by utilization of the Open Molecular Mechanics (OpenMM) library. Applications of the software to the conformational analysis of pentose sugars are discussed, in particular methyl beta-D-arabinoside will be considered.

***The Role of FCC Tetrahedral Subunits in the Phase Behavior
of Medium-Sized Lennard-Jones Clusters***

Ivan Saika-Voivod

Memorial University of Newfoundland

Louis Poon and Richard Bowles

University of Saskatchewan

The free energy of a 600-atom Lennard-Jones cluster is calculated as a function of surface and bulk crystallinity in order to study the structural transformations that occur in the core of medium sized clusters. We find the existence of number of structures based on the appearance of different sized FCC tetrahedral subunits.

Local Correlation Coupled-Cluster Methods Exploiting Cluster-in-Molecule Ansatz and Their Multi-Level Extensions

Piotr Piecuch

Michigan State University

Coupled-cluster (CC) theory has become the de facto standard for high-accuracy molecular calculations, but as all electronic structure approaches that aim at an accurate description of many-electron correlation effects, it faces a number of challenges. Among them are the prohibitive costs of CC calculations for larger molecular systems. To address this challenge, we have recently extended a number of CC methods, including the conventional CCSD and CCSD(T) approaches, and the size-extensive, left-eigenstate, completely re-normalized CC method with singles, doubles, and non-iterative triples, abbreviated as CR-CC(2,3), which is known to provide an accurate description of chemical reaction profiles involving single bond breaking and biradicals, to larger systems with hundreds of atoms through the use of the local correlation, cluster-in-molecule (CIM) ansatz. The resulting CIM-CCSD, CIM-CCSD(T), and CIM-CR-CC(2,3) methods are characterized by (i) the linear scaling of the CPU time with the system size when the same level of theory is applied to all CIM subsystems, (ii) the use of orthonormal orbitals in subsystem calculations, (iii) the natural coarse-grain parallelism, which can be further enhanced by the additional fine-grain parallelism of each subsystem calculation, (iv) the high computational efficiency, enabling calculations for large molecular systems at high levels of CC theory, (v) the purely non-iterative character of the local triples and other perturbative (e.g., MPn) corrections to correlation energy, and (vi) the applicability to the covalently and weakly bound molecular systems. In addition, one can use the flexibility of the CIM local correlation ansatz to mix different CC or CC and non-CC methods within a single calculation, enabling the rigorous formulation of multi-level local correlation theories that combine the high-level CC methods, such as CR-CC(2,3), to treat, for example, the reactive part of a large molecular system with the lower-order ab initio (e.g., MP2) scheme(s) to handle the chemically inactive regions without splitting it into ad hoc fragments and saturating dangling bonds. The performance of the CIM-CC approaches is illustrated by examining the bond dissociation curves in normal alkanes and alkyl radicals, the relative energetics of the water clusters, the diffusion of atomic oxygen on the silicon surface, the proton transfer in the aggregates of dithiophosphinic acids with the water molecules, and the Co-C bond dissociation in methylcobalamin.

The Nature of Molecular Hydrogen under Nano-Confinement: Insight from Theory and Simulations.

Tao Zeng, Hui Li, Robert Le Roy, and Pierre-Nicholas Roy
University of Waterloo

Water-hydrogen clusters are of particular interest for both fundamental and practical reasons. A better understanding of their nature has implications in astrophysics and in the field of hydrogen storage. The present research investigates the quantum dynamics of water-hydrogen clusters based on a new interaction potential, exact bound state calculations, and the Feynman Path Integral technique. We will first discuss on the development of reduced dimensional effective potentials for the description of the water hydrogen interaction. The quality of the potential is assessed via comparison to full dimensional bound state calculations for small clusters and comparison with the experimental rovibrational spectra. Secondly, we perform Path Integral Monte Carlo and Path Integral Molecular Dynamics simulations of larger clusters using our newly developed effective potential. We focus on the quantum delocalization effects of para-hydrogen and its superfluidity in the presence of water as the size of the hydrogen clusters grows. Spectroscopic observables will be computed and compared to available experiments. As an outlook, we will explore the potential impact of these effects on the behaviour of nano-scale water clathrates using recently proposed structures.

***Applications of Ring-Polymer Molecular Dynamics and Path Integral
Ground State Methods to He-CO₂ and Biomolecules***

Christopher Ing and Pierre-Nicholas Roy
University of Waterloo

Path integral molecular dynamics is an essential tool for computing static equilibrium properties of quantum mechanical systems. Using a generalization of this method, one can obtain approximate real-time quantum correlation functions. The theory of ring polymer molecular dynamics is briefly described and the dynamic properties are calculated using this method for both a model system and low temperature He-CO₂ with comparisons to exact theoretical calculations. Preliminary results investigating the temperature dependence of the dipole autocorrelation of a sugar is reported. Using a path integral ground state calculation, average ground state energies and structural properties can be computed. Ground state properties for a model system and He-CO₂ are presented as a proof-of-principle.

Effective Potential Approach to the Simulation of Large Para-hydrogen Clusters and Droplets

Jing Yang, Christopher Ing and Pierre-Nicholas Roy

University of Waterloo

The quantum simulation of large molecular system is a formidable task. We explore the use of effective potentials based on the Feynman path centroid variable in order to simulate large quantum clusters at a reduced computational cost. This centroid can be viewed as the “most” classical variable of a quantum system. Earlier work has shown that one can use a pairwise centroid pseudo-potential to simulate the quantum dynamics of hydrogen in the bulk phase at 25K and 14K [*Chem. Phys. Lett.* **1996**, 249, 231]. Bulk hydrogen, however, freezes below 14K and we rather focus on nanodroplets in the very low temperature regime in order to study the superfluid behaviour of hydrogen. The calculation of the effective potential will be discussed along with its use in the context of molecular dynamics simulations. Centroid structural properties will be presented and compared to the results of path integral Monte Carlo simulations. We will present an approach to deconvolute centroid structural properties in order to obtain real space results for hydrogen clusters of a wide range of sizes. The extension of the approach to the treatment of confined hydrogen will be discussed.

Superfluidity in Mixed Helium-Hydrogen Quantum Solutions Doped with a Chromophore Molecule

Hui Li, Robert Le Roy and Pierre-Nicholas Roy
University of Waterloo

Clusters of $\{\text{para}\}$ -H₂ had been predicted to exhibit superfluid behavior twenty years ago, but direct observation of this phenomenon has been elusive until our recent work combining experimental measurements and theoretical simulations of the non-classical rotational inertia and superfluid response of $\{\text{para}\}$ -H₂ clusters doped with CO₂. However, the size-dependent superfluid responses of these clusters reached a maximum at N=12, and the clusters become frozen at larger N. The present work examines the effect of adding a number of helium atoms to the pure $\{\text{para}\}$ -H₂ shell around a CO₂ chromophore, and investigating their effect on the superfluid response of CO₂-(pH₂)_N for N>12. This will help us understanding the role of helium as a "second solvent" species, and help explain the experiments that had been presented as evidence of superfluidity of doped hydrogen clusters embedded in helium nanodroplets. For this research, a ground-state path-integral code has been developed and will be applied in simulating doped cluster systems with molecular rotation; ground-state superfluid response theory is applied in these simulations. Such studies also provide a critical probe of the intermolecular forces, and can be used to test potential-energy surfaces. We recently determined multi-dimensional analytical 'Morse/Long-Range' potential energy surfaces for CO₂-H₂, CO₂-He, and H₂-He. The hindered-rotor averaging method is used in our reduced-dimension description for many-body interaction governing the present simulations.

- [1] P. Sindzingre, D.M. Ceperley, and M.L. Klein, *Phys. Rev. Lett.* **1991**, 67, 1871.
- [2] H. Li, R. J. Le Roy, P.-N. Roy, and A.R.W. McKellar, *Phys. Rev. Lett.* **2010**, 105, 133401.
- [3] S. Grebenev, B. Sartakov, J. P. Toennies, and A.F. Vilesov, *Science*. **2000**, 289, 1532.
- [4] H. Li, P.-N. Roy, and R. J. Le Roy, *J. Chem. Phys.* **2010**, 133, 104305.

Electric Field-Effects on Proton Transfer Kinetics in Formic Acid Dimer

Alya Arabi

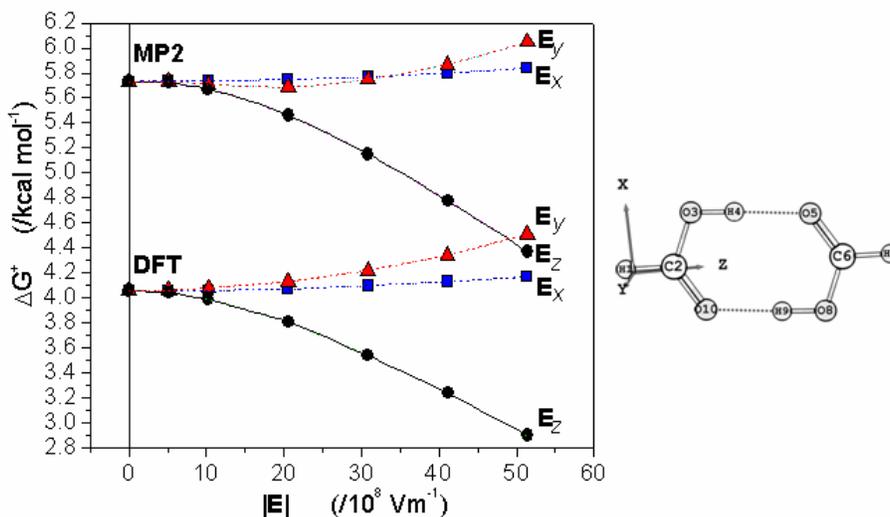
Dalhousie University

Chérif Matta

Dalhousie University and Mount Saint Vincent University

Critical biological molecules such as DNA or substrates in enzyme active sites can often be exposed to very strong local electric fields of the order of 10^8 - 10^{10} V/m. The effects of such fields on the rate constant (k) of the double-proton transfer reaction in the formic acid dimer are investigated [1]. This reaction constitutes a representative biochemical reaction that occurs under the influence of such fields and, more specifically, a simple model for the Löwdin mechanism of mutation in DNA base pairs. Barrier heights and shapes are calculated in the absence and presence of several static homogenous external fields (5.14×10^8 - 5.14×10^9 V/m) using density functional theory (DFT) and second order Møller-Plesset perturbation theory (MP2). Transition state theory followed by Wigner tunneling correction was applied to estimate rate constants (k). It is found that electric fields parallel to the long axis of the dimer lower the barrier height and considerably flatten the potential energy surface at the transition state region. The net effect is that the strongest fields studied increase k by a factor of ca. 3 - 4 (DFT/MP2) at 25°C. The figure depicts the formic acid dimer and the orientation of the x-, y- and z-axes. It also depicts the barrier heights (in kcal mol⁻¹) as a function of field strength in three orientations and two levels of theory.

[1] A. A. Arabi, C. F. Matta, submitted for publication (2011).



Investigation of Ionic Cluster Hydration with the Newly Parameterized Self-Consistent Charge Density-Functional Tight Binding Model

Soran Jahangiri

Concordia University

Grygoriy Dolgonos, Thomas Frauenheim

University of Bremen

Gilles Peslherbe

Concordia University

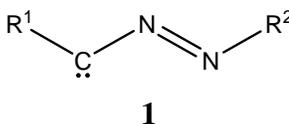
The investigation of ionic cluster hydration from first principles is usually restricted to small to medium-size clusters because of the prohibitive computational cost associated with ab initio quantum chemistry or density-functional theory (DFT) calculations for large clusters. The self-consistent charge density-functional tight-binding (SCC-DFTB) model has recently proven to be a reliable and computationally efficient approach to semiempirical DFT, and it thus allows routine investigation of much larger clusters than do first-principles methods. In this work, the parameter set of SCC-DFTB has been extended to include halogen atoms in order to investigate the cluster hydration of the anions of the Hofmeister series (CO_3^{2-} , SO_4^{2-} , F^- , CH_3COO^- , Cl^- , Br^- , NO_3^- , I^- , ClO_4^- , SCN^-). The extended SCC-DFTB is validated by comparing the geometries and binding energies predicted by the model for a series of small ionic aqueous clusters to the results of high-level ab initio quantum chemistry (MP2/aug-cc-pVTZ) and density-functional theory (PBE0/aug-cc-pVDZ) calculations. The accuracy of SCC-DFTB in predicting the geometries and binding energies of small ionic aqueous clusters, as well as its computational efficiency, make it a promising model for investigating much larger clusters, and even describing interatomic interactions for such systems in molecular dynamics simulations.

A Computational Investigation of Nitrilimine Cycloaddition Reactions

Sima Mehrpajouh, Gilles Peslherbe and Heidi Muchall

Concordia University

Nitrilimines (**1**) possess the general sequence $R^1C=NR^2$ and are described by six resonance structures, including allenic ($R-C=N=N-R$), dipolar and carbenic ($R-C=N=N-R$) contributions. The actual electronic structure of a nitrilimine is dictated by its substituents. All nitrilimines studied experimentally have been shown to undergo [3+2] cycloaddition reactions to dipolarophiles (alkenes and alkynes) to form 5-membered rings. In contrast, [1+2] cycloaddition reactions with unsaturated systems become possible for nitrilimines with a large carbenic resonance contribution. A Natural Resonance Theory (NRT) analysis of their electronic structure shows that the unsubstituted nitrilimine (HCNNH) has negligible carbenic character, while that of the NH_2 -disubstituted nitrilimine accounts for as much as 70%. Because of this carbenic character, [1+2] cycloaddition reactions with unsaturated systems become possible, in addition to the well-known [3+2] cycloaddition reactivity. For difluoronitrilimine, a species with moderate carbenic character (50% according to NRT), the [1+2] reaction is indeed favoured with an electron-poor alkene such as tetrafluoroethene, whereas the [3+2] reaction dominates for the relatively electron-rich ethene. These findings will be discussed and rationalized by Frontier Molecular Orbital theory.



Modeling of Percolation in Size Distributed Carbon Nanostructure Networks

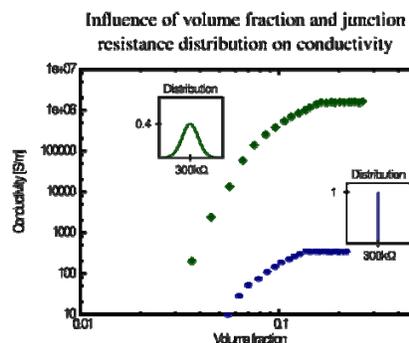
Louis-Philippe Simoneau and Alain Rochefort

Ecole Polytechnique de Montréal

Many photovoltaic and display devices rely on the use of transparent electrodes, which are generally rigid and brittle. Once a sufficient number of carbon nanotubes (CNTs) and graphene nanoribbon (GNRs) are connected to form a percolative network, their collective electronic and physical properties make these materials promising candidates for flexible transparent electrodes. The description of the underlying physics, along with an optimization of the characteristic of such nanostructures networks, can be efficiently addressed by computational means. Our understanding of the influence of the array structure on the final quality of the electrode can be improved by the modeling of charge transport in various networks, leading to a more selective optimization of their properties. Models for charge transport have already been developed for percolation systems with high aspect ratio CNTs, but they typically consider a single parameter to describe the CNT-CNT junctions [1]. However, in such complex materials, the propagation of charge carriers is usually limited by contact resistance that is a strongly dependent characteristic of the multiple network properties [2]. We have developed Monte Carlo (MC) algorithms to study the charge transport in bidimensional networks of CNT and GNR networks by incorporating realistic distributions and descriptions of CNT-CNT (or GNR-GNR) junctions. Our MC algorithms generate random networks with many controlled parameters which can be tuned to represent CNT mats, GNR mats, or other rod-like networks. We then evaluate the total conductance of the generated networks on the basis of individual contacts conductance, which in turn depend on the local network properties. Our results show that the length, diameter, orientation and chirality distributions within the percolative network of the CNT and GNR networks have a great importance on the resulting electrical performances.

[1] J. Hickset al., *Phy. Rev. E*, **2009**, 79.

[2] P. N. Nirmalraj et al., *Nano Lett.* **2009**, 9.



Band Alignment Optimization of rrP3HT/C₆₀ Bulk Heterojunction

Arnaud Maillard and Alain Rochefort

Ecole Polytechnique de Montréal

The cost limitation of traditional solar cells could be lifted by the development of organic solar cells using large-scale fabrication techniques associated with polymers. A better understanding of the electronic properties of the bulk heterojunctions (BHJs) constituting the active layer of the organic solar cells is required to increase the efficiency of this new generation of devices. DFT computations were used to study BHJs formed by the inclusion of C₆₀ in a regioregular poly(3-hexylthiophene) polymer (rrP3HT) crystal. Increasing the packing density in the BHJ extends the dipole induced at the rrP3HT-C₆₀ interface and the energy separation between the C₆₀-LUMO and the rrP3HT-HOMO, which is proportional to the open circuit voltage of the device (see Figure 1). This trend is consistent with the induced dipole moment variation observed at a pentacene-C₆₀ junction upon reduction of the intermolecular distance [1]. In contrast, increasing the size of rrP3HT crystal domains leads to a decrease of both the open circuit voltage and rrP3HT bandgap, in a similar fashion than upon the formation of rrP3HT crystallite along the annealing of BHJs (see Figure 2) [2].

[1] M. Linares, et al., *J. Phys. Chem. C*. **2010**, *114*, 3215.

[2] G. Dennler, et al., *Adv. Mater.* **2009**, *21*, 1323.

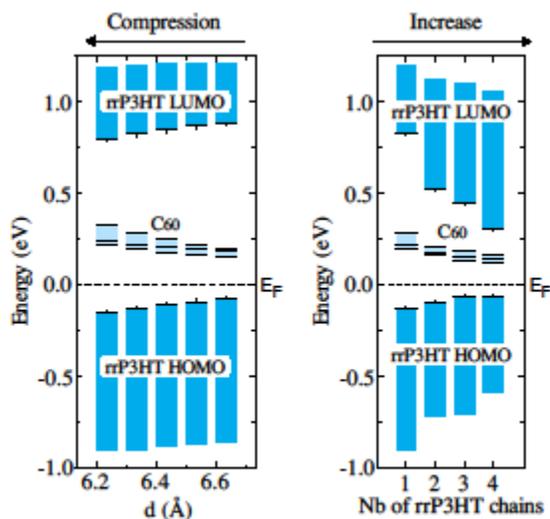


Figure 1

Figure 2

Determining the Structure of dialdehyde functionalized Cellulose Nanocrystals using Semi-Empirical Molecular Modelling.

Thomas Morgan, Theo van de Ven and Tony Whitehead
McGill University

The structure of dialdehyde cellulose is studied using semi-empirical Molecular Modeling. The structure is found to be less crystalline than cellulose. Dialdehyde cellulose shows intermolecular hydrogen bonding interactions holding the chains together as is the case for cellulose. Unlike in cellulose no hydrogen bonding is observed intramolecularly; this contributes to the reduced crystallinity of dialdehyde cellulose structures.

The Molecular Structure of Crystalline Cellulose using Ab-initio and PM6 Semi-Empirical Calculations

Kevin Conley, Theo van de Ven and Tony Whitehead
McGill University

The structure of nanocrystalline cellulose is studied using ab-initio Hartree-Fock and Semi-Empirical PM6 Molecular Modelling techniques. Two possible models of crystalline cellulose are studied: the existing flat geometry and a twisted geometry. After optimization of the energy, the flat molecule is energetically less stable than the twisted crystal which makes half a twist every seven glucose units (about 35 nm). Figure 1. Delocalized Molecular Orbitals (DLMOs) cover the whole flat crystal, reflecting the symmetry and show inter- and intra-molecular Hydrogen Bonds within certain DLMOs, Figure 2, top. There are no hydrogen bonds in the twisted crystal. Figure 1. Two chains of twisted cellulose 10 glucose unit long. Not twist at 7 glucose units. Figure 2. Two chains of flat cellulose 4 glucose units. Top view of DLMOs 105 (top left) and 115 (top right) of Network A. Energies = -1.383 a.u. and -1.364 a.u., respectively. These orbitals show an intermolecular (top left) and an intramolecular (top right) hydrogen bonds.

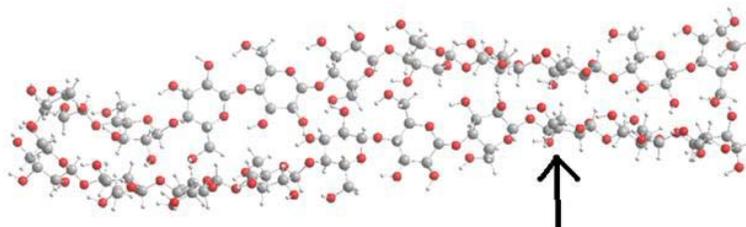


Figure 1.

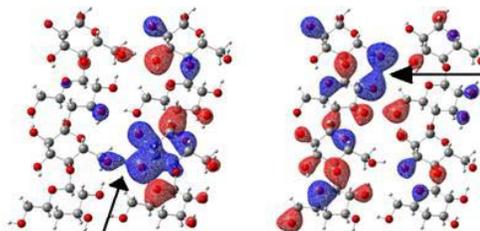


Figure 2.

Catalytic Mechanism of FK506-Binding Protein 35 with Tacrolimus

Corey MacDonald and Russell Boyd

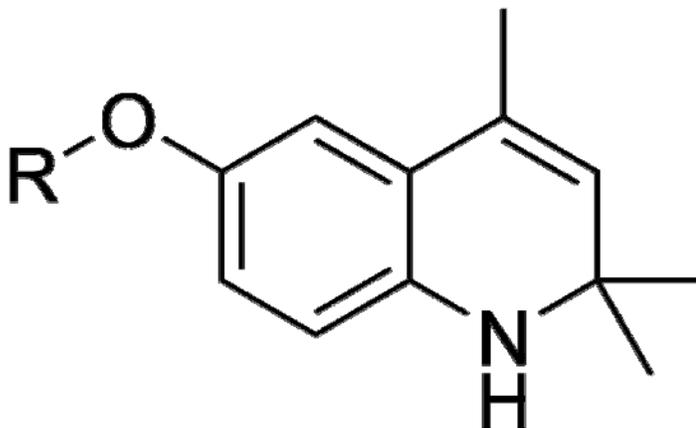
Dalhousie University

Peptidyl-prolyl cis/trans isomerases (PPIases) are a powerful enzyme superfamily capable of the rapid interconversion of cis and trans imide bonds involving proline amino acids in polypeptide chains. The PPIase that will be studied is FK506-binding protein 35 (FKBP35). FKBP35 is an active enzyme in *Plasmodium falciparum* and *Plasmodium vivax*, two major species of protozoan parasites responsible for malaria transmission. The process under investigation is the reaction mechanism of FKBP35 and FK506 (also known as tacrolimus). Tacrolimus has been shown to have anti-malarial activity, as it binds to FKBP35 and prevents the enzyme from folding protozoan proteins, thus preventing the life cycle of the parasite. Using previously obtained NMR and crystallographic data on tacrolimus-bound FKBP35, the geometry optimized enzyme-substrate complex was computed. This was done using QM/MM simulations, with B3LYP/6-311G+G(d,p) used to model the active site, and the AMBER force field used for the remainder of the system. The nonstandard residue atoms, including tacrolimus atoms, were calculated using the RESP protocol implemented in the AMBER11 package following electrostatic potential calculations at the HF/6-31G* level of theory.

*Reaction of Group 16 Analogues of Ethoxyquin with Hydrogen Peroxide,
a Computational Study*

Sean Collins, Gavin Heverly-Coulson, and Russell Boyd
Dalhousie University

Organoselenium compounds that mimic the behaviour of the antioxidant enzyme glutathione peroxidase (GPx) have been studied for a quarter century as a way to protect tissue from oxidative damage. It has been known for many years that organosulphur compounds are less efficient at reducing peroxides than their organoselenium counterparts. More recently it has been found that replacing selenium with tellurium produces even better antioxidant compounds. In this work, we study the reaction of the ethoxyquin molecule, and its other group 16 analogues, with hydrogen peroxide using electronic structure calculations. This series of molecules has been observed experimentally to show remarkable increases in GPx activity as the chalcogen atom is varied. Through computational modelling, we examine the mechanism of this reaction to better understand this phenomenon.

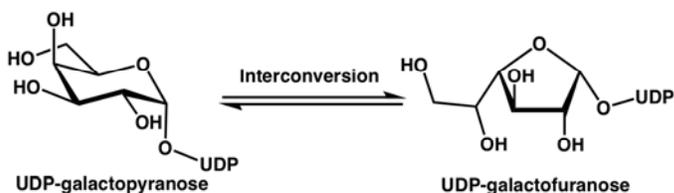


Mechanism Study of FAD Catalyzed UDP -Galactopyranose Mutase Processes: QM/MM and DFT Investigations

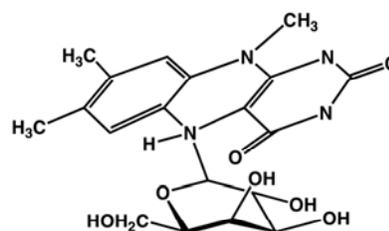
WenJuan Huang and James Gault

University of Windsor

Bacteria possess a cell wall that is integral to their survival. Importantly, eukaryotic cells, e.g., as in mammals, do not have such walls. UDP-galactopyranose mutase (UGM) is a key enzyme involved in their biosynthesis in pathogenic bacteria such as *K. pneumoniae*, and *M. tuberculosis*. Consequently, there is great interest in understanding how these enzymes function, so as to develop UGM-specific therapeutic drugs. UGM is a flavin (FAD) containing enzyme that catalyzes the interconversion of galactopyranose (Galp) and galactofuranose (Galf), i.e., interconversion of galactose's 6 and 5-membered ring forms. (Scheme 1). Recently, a novel covalent bond has been reported to form during the mechanism between the FAD cofactor and the substrate. (Scheme 2) Unfortunately, despite detailed experimental studies, little remains known about the exact mechanism. We have used QM/MM and DFT-based approaches to investigate the mechanism of UGM.



Scheme 1



Scheme 2

Semi-empirical Molecular Modelling of Picloram Specific Antibody

Mohidus Samad Khan, Tony Whitehead and Theo van de Ven
McGill University

Picloram (4-amino-3,5,6-trichloropyridine-2-carboxylic acid), a herbicide used to kill unwanted plants, enters the fresh water supply and cause Health and Environmental problems. Picloram has a very long life-time and is considered mildly toxic to birds and mammals and moderately toxic to aquatic species. The Environmental Working Group (EWG) reports that people are consuming water, contaminated with Picloram and other Herbicides, in Western Countries. Paper based Sensors can be used to detect, and filters to remove Picloram from Contaminated Water. Researchers have developed a filtration system by fusing an Anti-Picloram Antibody Fragment to Pulp Fibre to remove Picloram. In this paper the Picloram interaction with the specific antibody is Modelled using Quantum Chemistry. A Semi-empirical Quantum Method (PM3) is used to model a) Picloram, b) Amino acids as antibody building blocks and c) Complementary Determining Regions (CDR) of Picloram antibody. Antibody CDRs are regions within an Antibody which complement an antigen's shape. Delocalized Molecular Orbitals (DLMO), Bond Lengths, Bond Angles, Total Charge, Dipole Moments, Electrostatic Potential Surface, etc. are calculated and analyzed to elucidate the binding characteristics of Picloram to the Anti-Picloram CDRs. DLMOs, in particular Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO), comprehend the binding-site, bond affinity and specificity of Picloram to the Anti-Picloram antibody. These calculations will illuminate the morphology of Antigen-Antibody interactions on paper and will help to develop bioactive filter papers and paper sensors to assist in health and environmental problems.

ABSTRACTS

Posters

Interaction of Poly-Peptides with Denaturants as a Possible Model to Investigate the Mechanism of Protein Denaturation

Xijun Wang and Gilles Peslherbe

Concordia University

Proteins can undergo denaturation, losing their tertiary structure and secondary structure, upon applying external stress or mixing with chemical species such as strong acids or bases, inorganic salts or organic molecules. The guanidinium ion is one of the most powerful such denaturants. However, the precise mechanism through which the protein is denatured by guanidinium is still unresolved. In fact, both a direct mechanism (involving direct protein-denaturant contact that results in the protein structure breakdown) and an indirect mechanism (involving protein conformational change due to denaturant-induced changes in the structure and dynamics of the hydrating water) have been proposed. In order to attempt to address this issue, the mixing of highly charged homo-poly-peptide (poly-lysine, pH=7) with guanidinium chloride has been investigated as a model of protein denaturation by guanidinium [1]. However, no definite conclusion was reached from the experimental data regarding the mechanism of protein denaturation. In this contribution, we discuss a number of reported features, from the crystal structure of poly-lysine [2] to the FTIR signature of β -sheets [3], that point towards an indirect mechanism of how guanidinium affects the secondary structure of poly-lysine. Basically, hydration of highly concentrated guanidinium would decrease the amount of water available to solvate the peptides, leading to an ordering of the poly-peptide structure. First-principles simulations to examine this hypothesis and the relevance of the guanidinium-peptide model to address protein denaturation are discussed.

[1] Esposito, C. *Investigation of the interaction of GdnHCl with poly-L-lysine, horseradish peroxidase and Cytochrome c monitored via FTIR, CD and fluorescence spectroscopies*. Thesis, Concordia University, Montreal, **2000**.

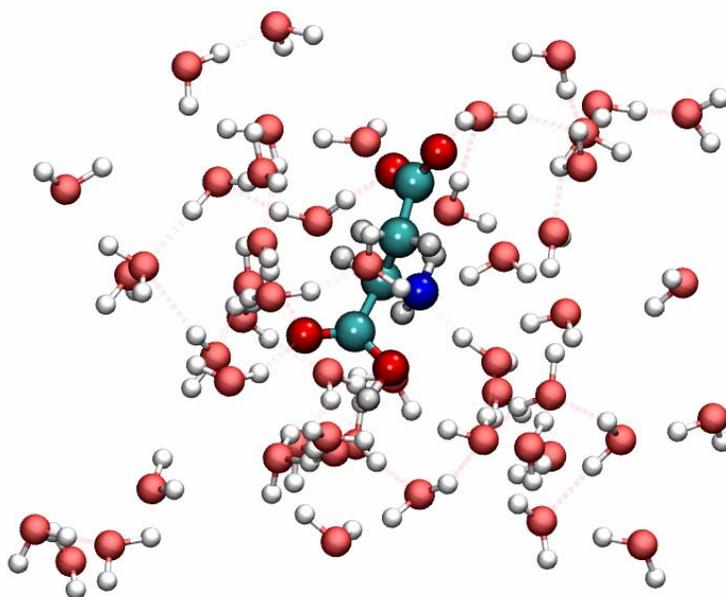
[2] Dos, A.; Schimming, V.; Tosoni, S.; Limbach, H. H., *J. Phys. Chem. B.* **2008**, *112*, 15604-15615.

[3] Maurer, A.; Lee, G., *Eur. J. Pharm. Biopharm.* **2006**, *62*, 131-42.

***Trends in Hydrogen Bonding within the Solvation Shells of Amino Acids:
An Ab Initio Molecular Dynamics Study***

Laura Albrecht and Russell Boyd
Dalhousie University

Solvent effects can be used to explain protein residue interactions, such as the formation of secondary structures that hide hydrophobic side groups and the folding patterns adopted by specific amino acid sequences. The implicit and explicit solvation methods used to represent a solvent environment in many protein folding simulations do not include the quantum nature of the hydrogen bonds present in water, which may contribute to their inability to predict protein folding. We present here an evaluation of the hydrogen bond structure within the first two solvation shells of the amino acids, derived from Car-Parrinello molecular dynamics calculations. By evaluating the systems from first principles we are able to accurately represent each hydrogen bond's contribution to the final energy and structure of the solvent water shell. We focus on the trends observed across a series of amino acids in order to understand the specific contribution of various functional groups toward the structure of the surrounding waters. The goal is to better understand how a protein's folding process affects its solvation shell, based on the exposure or concealment of the functional groups that are present. This will help characterize the solvent's role in the mediation of protein folding.



Heterogeneous Condensation of the Lennard-Jones Vapor Onto a Nanoscale Seed Particle

Levent Inci and Richard Bowles
University of Saskatchewan

The heterogeneous condensation of a Lennard-Jones vapor onto a nanoscale seed particle is studied using molecular dynamics simulations. Measuring the nucleation rate and the height of the free energy barrier using the mean first passage time method shows that the presence of a weakly interacting seed has little effect on the work of forming very small cluster embryos but accelerates the rate by lowering the barrier for larger clusters. We suggest that this results from a competition between the energetic and entropic features of cluster formation in the bulk and at the heterogeneity. As the interaction is increased, the free energy of formation is reduced for all cluster sizes. We also develop a simple phenomenological model of film formation on a small seed that captures the general features of the nucleation process for small heterogeneities. A comparison of our simulation results with the model shows that heterogeneous classical nucleation theory provides a good estimate of the critical size of the film but significantly overestimates the size of the barrier.

*Using a Genetic Algorithm to Investigate
the Structure of Samarium-Doped Ceria*

Arif Ismail, James Hooper, Javier Giorgi and Tom Woo
University of Ottawa

Solid oxide fuel cells (SOFCs) are an attractive solution to the energy crisis due to their efficiency and low operating temperature [1,2]. Of particular interest is the solid electrolyte, which conducts O_2^- ions from the cathode to the anode. A material known as samarium-doped ceria (SDC) has high oxygen ion conductivity and thus is the electrolyte of choice in today's methane-fuelled SOFCs [1,2]. Yet, without a physical understanding of the factors that influence ionic conductivity in doped ceria, it remains impossible to design better materials for SOFCs. With this goal in mind, a few atomistic simulations of SDC have been published to date. However, these works investigate only low dopant concentrations of the bulk oxide (~3%), while it is known that SDC is used in fuel cells at much higher concentrations (~11%) [3-5]. The challenge of simulating realistic concentrations stems from the enormous number of available structures. For example, for 6.6 % SDC there are 3.5 billion possible ways to place the Sm ions and the oxygen vacancies in a 94-atom simulation cell. In this work [6], we circumvent the problem by developing a genetic algorithm to search the structural space of samarium-doped ceria for the most energetically stable configuration which will predominate in low temperature fuel cells. We first establish the effectiveness of our algorithm with 3.2 % SDC, as it recovers the same results as a systematic search. With both classical and DFT+U simulations, we use our genetic algorithm to find the lowest-energy configurations of 6.6 % and 10.3 % SDC, which are impossible to investigate systematically. Our extensive structural evaluation provides researchers with the specific configurations necessary to study diffusion pathways at realistic concentrations of SDC, and provides insight on the influence of dopant-vacancy interactions on the ionic conductivity of doped ceria.

- [1] *J. Power Sources*. **2003**, 122, 122
- [2] *Electrochem. Commun.* **2009**, 11, 1508.
- [3] *PNAS*. **2006**, 103, 3518
- [4] *Solid State Ion.* **2009**, 180, 13
- [5] *Phys. Chem. Chem. Phys.* **2009**, 11, 3241
- [6] *Phys. Rev. B*. **2010**, 81, 224104.

Poster 5

Ground-state Properties of LiH by Reptation Quantum Monte Carlo



Egor Ospadov, Daniel Oblinsky and Stuart Rothstein
Brock University

We apply reptation quantum Monte Carlo to calculate one- and two-electron properties for ground-state LiH, including all tensor components for static electric polarizabilities and hyperpolarizabilities to fourth-order in the field. We present formulas for the electrical response properties free from the finite-field approximation, which can be problematic for the purposes of stochastic estimation. The importance sampling is done using a single determinant HF-SCF wave-function with a large (QZ4P) STO basis set, generated using a commercial software package, hence allowing us to omit the use of many-parameter Jastrow-type functions of the inter-electronic and inter-nuclear distances and remove any computational overhead associated with them. Our results for accurately known properties, such as the energy and the dipole moment, are of high quality and in good agreement with the literature. Our polarizability values are consistent with the literature, albeit with a few exceptions in which the literature has wide disagreement as well. E. Ospadov, D. G. Oblinsky, S. M. Rothstein, *Phys. Chem. Chem. Phys.* **2011**, *13*, 8031.

***Conformational Mobility in Cytochrome P450 from Piezophilic Bacteria
Photobacterium Profundum SS9***

Liliya Shamova

Kazan Federal University

Anastasia Bakulina

State Research Center of Virology and Biotechnology Vector

Elena Sineva

University of California San Diego

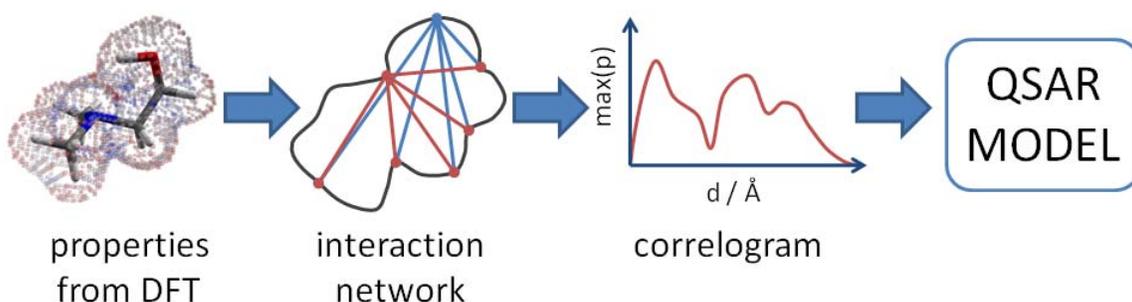
The role of high-pressure adaptation is especially important in the case of cytochromes P450 whose functional mechanisms involve hydration-dehydration dynamics. Fine-tuning of water accessibility of the active site and its synchronization with substrate binding, electron transfer and product release are of vital importance for P450 catalytic efficiency. Cytochrome P450 from deep-sea bacteria *Photobacterium profundum* SS9 (P450-SS9) is a putative fatty acids hydroxylase. Recently, the existence of the equilibrium between “open” and “closed” states of the protein was shown. The “closed” conformation exhibits restricted water accessibility to the heme pocket [1]. However, the structural mechanisms underlying open-to-close state transition are still unknown. In this study, the three-dimensional model of P450 SS9 was constructed using the homology modeling. Palmitic and myristic acids, P450-SS9 type I ligands, were docked into the active site. To refine docking results and to address the conformational space of the protein, molecular dynamics in GROMACS and 53a6 force field was employed. The results show that conformational changes in active site occur upon ligand binding.

[1] E.V. Sineva, D.R. Davydov, *Biochemistry*. **2010**, *49*, 10636.

***Exploration of Electronic Structure Based Descriptors for 3D QSAR
Models of Asymmetric Catalysis***

Nicholas Trefiak and Tom Woo
University of Ottawa

In this poster we present some recent work on using Quantitative Structure Activity Relationships (QSAR) for catalyst optimization. QSAR is a common tool in the pharmaceutical industry for identifying which aspects of a drug are responsible for its biological activity, and only in the past few years has the method been applied to catalytic problems. We examined 18 catalysts used for the asymmetric addition of diethylzinc to benzaldehyde, ranging in %e.e. from 0 to 98%. Unique to our study, we utilized quantum chemically derived descriptors to relate the catalysts' enantioselectivity to their QM properties. Gaussian09 was used to calculate the total electron density, electrostatic potential, HOMO, and LUMO. The quantum chemical data at the van der Waals surface was treated with a data reduction method to generate so-called "correlograms" which form the descriptors for the catalyst. Each correlogram acts like a "fingerprint" describing a specific catalyst. Partial least squares regression was used to find correlations between these "fingerprints" and catalyst enantioselectivity. A QSAR model with $R^2 = 0.925$ and $Q^2(\text{leave-one-out}) = 0.826$ for three latent variables was obtained.



Poster 8

Mapping Approach to Quantum-Classical Dynamics

Ali Nassimi

University of Calgary

Studying the time evolution of any system large enough to be of any biological or condense matter significance is computationally intractable. In this presentation, we show how one can simulate the dynamics of a condense matter system using Hamilton's equations of motion while keeping many of the quantum effects in the dynamics. This is done by means of few mathematical transformations and two approximations. These include a partial Wigner transformation (casting part of the system in the phase space), the quantum-classical approximation (assuming part of the system to behave classically), representation in the subsystem basis, mapping over fictitious harmonic oscillators, partial Wigner transformation over the rest of the system and neglecting a portion of the effect of classical bath over quantum subsystem.

*Theoretical Studies of Electron Solvation
in Photoexcited Iodide-Solvent Clusters*

Chun Mak and Gilles Peslherbe
Concordia University

The photoexcitation of halides dissolved in polar liquids results in the formation of charge-transfer-to-solvent (CTTS) states which are precursors to the solvated electron, a species involved in numerous important chemical and biological processes. Iodide-polar solvent clusters, $I(S)_n$, where S represents solvent molecules, possess analogous CTTS excited states which relax to produce solvated electron clusters $(S)_n^-$. Numerous ultrafast experiments have been performed to investigate this relaxation process, but its molecular details remain unclear. In this contribution, the solvation structure and CTTS excited states of $I(S)_n$ (S = H₂O, NH₃ and CH₃OH) are characterized with reliable quantum chemical calculations to understand the role played by individual solvent molecules and the iodine atom in supporting excess electrons ejected from solvated halides. First-principles molecular dynamics simulations are then used to elucidate the molecular details of the electron solvation process in photoexcited $I(S)_n$. New insights into the properties of the solvated electron in various polar liquids arising from the present work will be discussed.

Computer Simulations of O₂ Diffusion in the Human Hemoglobin Tetramer

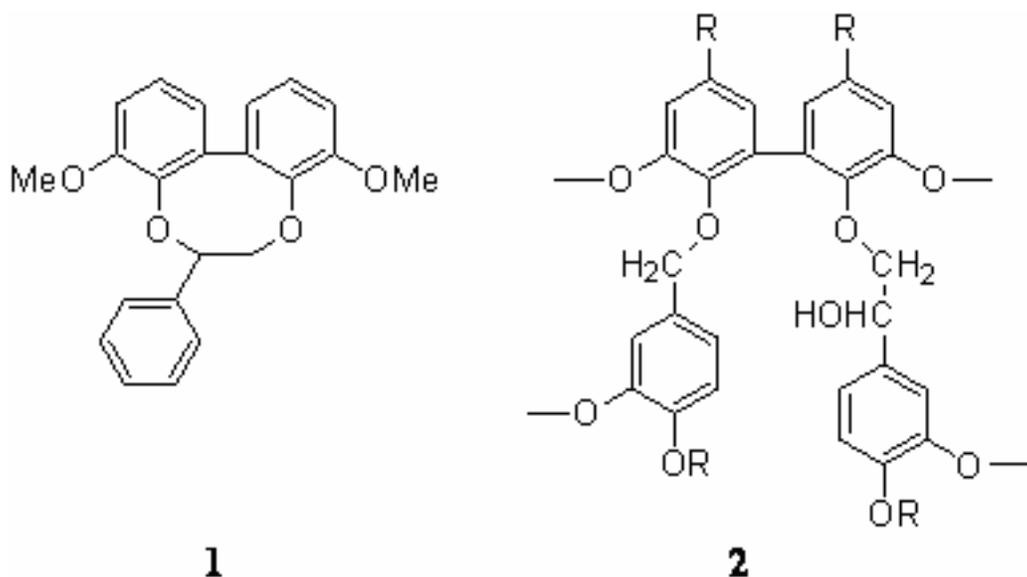
Mariya Shadrina, Ann English and Gilles Peslherbe
Concordia University

The diffusion of small-molecule substrates or ligands within protein matrices is a critical biochemical process. Tunnels within the macromolecule are designed to promote substrate/ligand diffusion to special binding sites, a process that pivotally defines biochemical specificity and reactivity. Computer simulations can reveal details of the small-molecule interactions with proteins that are impossible to observe experimentally. The focus of this contribution is the hemoglobin tetramer (Hb), the highly abundant O₂⁻ binding protein in red blood cells. The cooperative binding of O₂ to Hb, which facilitates O₂ delivery from the lungs to the tissues, depends on a conformational transition of the globin from a low-affinity, unligated T-state to a high-affinity, ligated R-state. Since we are interested in the complex interplay between the conformational states of Hb and its interaction with small ligands such as O₂ and NO we considered several Hb tetramer models: T-state deoxyHb, R-state deoxy Hb and R-state oxyHb. Computer simulations of O₂ diffusion performed in this study revealed detailed information about the O₂ diffusion pathways, exit points, sterical barriers along diffusion tunnels and highly-accessible ligand docking sites within the alpha- and beta-subunits. Obtained results demonstrate the completely different organization of diffusion tunnels within the alpha- and beta-subunits of the Hb tetramer with similar structure of their distal sites. Two identical gates were indicated in both subunits: B10E11G8 and E7 (distal His). This structural motif widely spread among globins plays an important role in the control of diffusion kinetics and dynamics influencing the ligand affinity. The former guides ligands to the protein interiors where ligands can escape to the solvent (long exit paths), whereas the latter controls ligand escaping from protein via the short exit paths. Returning to the debates about contribution of alternative (long) exit paths we showed that significant part of ligands escapes from the protein via the long exit paths especially in the beta-subunit. Results obtained in this study are in excellent consistent with known experimental data and reveal new insight on ligand diffusion within Hb.

Exploratory Computational Studies Towards the Photo-Induced Degradation of Lignin

Lei Zhang, Gilles Peslherbe and Heidi Muchall

Lignin is a three-dimensional phenolic polymer and is amongst the most abundant biopolymers on earth. The photo-induced degradation of lignin is an important and complicated process, through which phenoxy radicals are produced via different pathways and may be further oxidized into quinones causing photo-yellowing. While the contribution of different pathways is still under debate, their roles in the photo-induced yellowing of lignin-rich, high-yield, mechanical pulps are also ambiguous. In this work, we approached these studies by evaluating the photo-induced fragmentation of dibenzodioxin (1) and its biphenyl derivative (2), which are highly photo-sensitive structural elements involved in chemical pulping and bleaching, using a computational approach validated for acetone photolysis.



A New Basis for Computing Rovibrational Spectra of Polyatomic Molecules

Xiao-Gang Wang and Tucker Carrington Jr.
Queen's University

To ensure that all matrix elements are finite, it is common when solving the rovibrational Schroedinger equation, to use a basis of products of vibrational and rotational functions with vibrational functions that depend on a rotational quantum number, K . To treat large amplitude motion, it is convenient to use products of spherical harmonics for the bend part of the vibrational functions and it is the spherical harmonics that are K dependent. This shared-index basis has been the basis of choice for computing rovibrational levels of molecules undergoing large-amplitude motions. However, the shared K index makes contracted basis calculations more difficult. This problem is obviated by using basis functions that are products of vibrational and rotational functions with vibrational functions that are independent of rotational quantum numbers. The spherical harmonics of the vibrational functions are K -independent. In this poster we present this new product basis of spherical harmonics and Wigner functions. With this new basis we have the best of both worlds: we can deal with large amplitude motion because we use spherical harmonics and we can contract efficiently. In the new basis, some matrix elements are infinite but this causes no problems as long as the two embedding vectors defining the body-fixed axes for rotation are not linear. The new basis is used to compute rovibrational levels of H_2O_2 and the results are identical with the benchmark results obtained with the non-direct product basis.

*Semi-Empirical Quantum Models for Chemical Reactions
in Zinc Metalloenzymes*

Shihao Wang and Guillaume Lamoureux
Concordia University

Semi-empirical quantum models are widely used in mechanistic studies of organic reactions. They have been used in prediction of the activity of metalloenzymes, refinement of metalloprotein structures, and discovery or validation of new metal-binding sites. The most commonly used semi-empirical quantum models are based on the neglect of diatomic differential overlap (such as AM1, RM1 and PM3). The performance of these models heavily depends on the parametrization procedure and the training set. Since those models were generally parametrized from small organic molecules, they are not accurate enough for zinc-catalyzed reactions in enzymes. We have developed a new methodology for system-specific parametrization of semi-empirical quantum models that can be used to study hydrolysis reactions in zinc metalloenzymes. The training set is prepared by high level ab initio data, which includes fragments of the enzyme active sites. A scoring function is defined by the most important properties, such as bond lengths, angles, proton affinities, hydrogen bond energies, reaction energies and barriers. The parametrization process contains random searching in the parameter space and minimization of the scoring function. This process is repeated for each element until the parameters are converged. The final parameter set is tested in quantum mechanical / molecular mechanical (QM/MM) simulations, and is compared with the original AM1 models.

List of Participants

Laura Albrecht	Dalhousie University
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Stephane Bedwani	Ecole Polytechnique de Montréal
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Kevin Conley	McGill University
Stephen Constable	University of Waterloo
Javier Cuervo	University of Calgary
Tom Daff	University of Ottawa
Ann English	Concordia University
Barbara Goodall	Saint Mary's University
Ian Hamilton	Wilfrid Laurier University
Gavin Heverly-Coulson	Dalhousie University
WenJuan Huang	University of Windsor
Levent Inci	University of Saskatchewan
Christopher Ing	University of Waterloo
Arif Ismail	University of Ottawa
Soran Jahangiri	Concordia University
Jean-Francois Jobidon	Ecole Polytechnique de Montréal
Raymond Kapral	University of Toronto
Mohidus Samad Khan	McGill University
Guillaume Lamoureux	Concordia University
Hui Li	Jilin University and University of Waterloo
Corey MacDonald	Dalhousie University
Arnaud Maillard	Ecole Polytechnique de Montreal

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Heidi Muchall	Concordia University
Ali Nassimi	University of Calgary
Egor Ospadov	Brock University
Gilles Peslherbe	Concordia University
Piotr Piecuch	Michigan State University
Bianca Provost	University of Ottawa
Enrico Purisima	Biotechnology Research Institute (NRC)
Alain Rochefort	Ecole Polytechnique de Montréal
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Pradeep Varadwaj	Concordia University
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