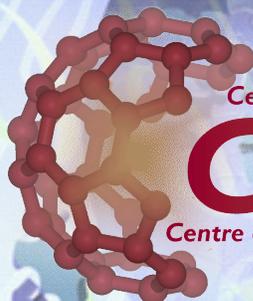


12th Annual CERMM Symposium

May 12, 2012

Concordia University, Montréal



Centre for Research in Molecular Modeling

CERMM

Centre de recherche en modélisation moléculaire



Symposium Program

Saturday, May 12, 2012. Richard J. Renaud Science Complex, SP-S110

9:45 Welcoming remarks

Gilles Peslherbe, Director, Centre for Research in Molecular Modeling

Discussion Leader: **TBA**

9:50 **Holger Vach** (CNRS - Ecole Polytechnique)

Aromatic silicon nanoclusters

10:30 **Kevin Conley**, Theo van de Ven, and Tony Whitehead (McGill University)

Theoretical study of self-assembly of cellulose derivatives

10:50 **Esam Orabi** and Guillaume Lamoureux (Concordia University)

Complexation of cations with aromatic amino acid side chains: QM and MM investigations in gas phase and in aqueous solution

11:10 **Coffee Break**

Discussion Leader: **TBA**

11:30 **Daniel Borgis** (Ecole Normale Supérieure)

A particle-based implicit solvent model for biosimulations

11:50 **Marat Talipov**, Dmitry Khomyakov, and Qadir Timerghazin (Marquette University)

Making S-nitrosothiols click: Computational design of selective reagents for SNO-proteomics based on a novel (3+2)-cycloaddition reaction

12:10 Marat Talipov, Dmitry Khomyakov, and **Qadir Timerghazin** (Marquette University)

Bioactive compounds with antagonistic resonance structures: Computational predictions of protein control

12:30 **Lunch**

Discussion Leader: **TBA**

13:50 Nicholas Mosey (Queen's University)

First-principles simulations of tribological processes

14:30 Parisa Akhshi and Gang Wu (Queen's University)

Molecular dynamics simulations of ion transport in G-quadruplex DNA Structures (ion channels)

14:50 Mohammad Ashtari and Natalie Cann (Queen's University)

Poly-proline based chiral stationary phases: A molecular dynamics study of structure, solvation and selectivity

15:10 Coffee Break

Discussion Leader: **TBA**

15:30 Oleksiy Khavryuchenko (Kyiv National Taras Shevchenko University)

Antiferromagnetic ordering in the conjugated chains of disordered postpolymeric carbon: a case DFT investigation

16:10 Christopher Daub and Natalie Cann (Queen's University)

Evaporation and condensation of small charged clusters of water and methanol

16:30 Vibin Thomas, Ugo Rivard, and Radu Iftimie (Université de Montréal)

Concerted and sequential proton transfer mechanism in water-separated acid-base encounters pair in aqueous solution

17:00 Poster Session and Reception sponsored by Azuris Technologies Inc.

Poster Presentations

1. *Structural and thermodynamic characterization of the first oligomeric structures of Human Amylin using Coarse-grained Replica Exchange Molecular Dynamics simulations*
Saïd Bouzakraoui and Normand Mousseau (Université de Montréal)
2. *Sulfate patterns in water at long distance: Spectral signature and structure with first-principles modeling*
Xijun Wang, Soran Jahangiri, and Gilles Peslherbe (Concordia University)
3. *Accounting for polarization in molecular wires with self-consistent Huckel theory*
Randall Dumont (McMaster University)
4. *Computational study of weak interactions in the stabilization of unfavourable tert-butyl substituted cyclohexane conformers*
Philippe Archambault and Heidi Muchall (Concordia University)
5. *Ground-state properties of LiH by Reptation Quantum Monte Carlo*
Matthew Flister, Marat Talipov, and Qadir Timerghazin (Marquette University)
6. *Electrogenic transport mechanisms in ammonium transporters*
Shihao Wang and Guillaume Lamoureux (Concordia University)
7. *Computational investigation of the hydration of alkyl diammonium chlorides and their effect on the water/organic phase separation*
Soran Jahangiri, Sean Mercer, Philip Jessop, and Gilles Peslherbe (Concordia University)
8. *Simulations of charge-transfer-to-solvent dynamics in photoexcited iodide-methanol clusters*
Chun Chi Mak and Gilles Peslherbe (Concordia University)

ABSTRACTS

Talks

*Aromatic silicon nanoclusters***Holger Vach**

École Polytechnique (France)

We report a new nano-crystalline form of silicon that gives birth to pure hydrogenated silicon nanoclusters that absorb light in the ultraviolet, visible and infrared spectral region despite their small size of only 1nm and without the need for expensive or toxic metal atoms. Based on first-principles calculations, we demonstrate that those pure, but over-coordinated silicon nanocrystals are more stable than any other known silicon clusters due to electron delocalization and that they form spontaneously via self-assembly. Therefore, we predict their immediate application in fields ranging from photovoltaic and light emitting devices to photothermal cancer treatment.

Theoretical study of self-assembly of cellulose derivatives

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

Novel cellulose derivatives functionalized with phenyl and imide groups were studied using semi-empirical PM6 calculations. The phenyl groups were positioned in orientations favorable for self-assembly into larger structures. The delocalized molecular orbitals showed the interactions are driven by π -stacking between the phenyl groups and hydrogen bonding between the imide chains.

***Complexation of cations with aromatic amino acid side chains:
QM and MM investigations in gas phase and in aqueous solution***

Esam Orabi and Guillaume Lamoureux
Concordia University

Cation- π interactions are non-covalent interactions known to play important roles in stabilization of protein structures, molecular recognition, and in protein-ligand interactions. Cation- π interactions are contributing to the binding of quaternary ammonium ligands (RNH_3^+ or $\text{RN}(\text{CH}_3)_3^+$) to various protein receptors, and are also likely involved in the blockage of potassium channels by tetramethylammonium (TMA^+) and tetraethylammonium (TEA^+). Owing to their importance for protein-ligand interactions, polarizable molecular models for NH_4^+ , TMA^+ , and TEA^+ interacting with model compounds for aromatic amino acids side chains (phenylalanine, tyrosine, tryptophan) are optimized. The models are adjusted based on the ab initio properties of the complexes at the MP2(full)/6-311++G(d,p) level of theory. The models are used in molecular dynamic simulations to investigate the binding geometry and the binding free energy between the cation- π pairs in aqueous solution. The results are showing that while the binding strength between the three cations and a given aromatic compound in the gas phase follows the trend $\text{NH}_4^+ > \text{TMA}^+ > \text{TEA}^+$, the binding affinity is reversed in aqueous solutions.

*A particle-based implicit solvent model for biosimulations***Daniel Borgis**

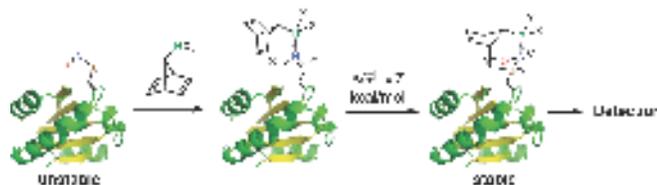
Ecole Normale Supérieure (France)

To describe solvation effects in all-atom (AA) as well as coarse-grained (CG) molecular dynamics simulations, a numerically efficient coarse-grained water model is introduced. The solvent is represented by polarizable pseudo-particles embedding roughly one (AA) or three (CG) water molecules. The particles carry induced dipoles that are made sensitive to the solute electric field, but not to each other, by a proper renormalization of the local polarizabilities. The solvent model is compatible with atomistic force fields, and a coarse-grained proteins force field involving a reduced number of grains per residue and yields quantitative description of solvation properties, such as hydrophobic forces and electrostatic solvation free-energies. Those later quantities can be estimated "on-the-fly" over short simulation windows. This is illustrated for the hydration of peptides, proteins, and nucleic acids.

Making S-nitrosothiols click: Computational design of selective reagents for SNO-proteomics based on a novel (3+2)-cycloaddition reaction

Marat Talipov, Dmitry Khomyakov, and Qadir Timerghazin
Marquette University (USA)

In this contribution, we computationally demonstrate that S-nitrosothiols (RSNOs) can undergo hitherto unknown (3+2)-cycloaddition reactions with alkynes and alkenes. Although non-activated RSNO cycloaddition reactions have high activation energies (21–23 kcal/mol at the CBS-QB3 level), the reaction barriers can be dramatically lowered by coordination of a Lewis acid to the N atom of the –SNO group. To exploit this effect, reagents were designed with dipolarophile and Lewis acid moieties linked by a rigid scaffold. Based on this approach, prototype RSNO labeling reagents with predicted activation enthalpies less than 5 kcal/mol and reaction exothermicities more than 40 kcal/mol were proposed. These reactions can efficiently convert the unstable –SNO group into a stable species and so may have a great potential for the proteomic analysis of S-nitrosated proteins. The importance of the conceptual understanding of the electronic structure in the design of novel RSNO cycloaddition reactions will be highlighted.



***Bioactive compounds with antagonistic resonance structures:
Computational predictions of protein control***

Marat Talipov, Dmitry Khomyakov, and Qadir Timerghazin
Marquette University (USA)

Resonance structures is perhaps the oldest and a truly chemical way to represent molecules with complex electronic structure and to rationalize/predict their reactivity. Recently, we identified an interesting class of compounds whose resonance description requires inclusion of two resonance components that imply diametrically opposite formal charge distributions and chemical reactivities. Due to the difference in charge distributions, even small changes in environment or substituent effects can affect the relative contributions of these antagonistic resonance structures. This electronic structure modulation can lead to profound changes in molecular properties and chemical reactivity. An excellent example of resonance-antagonistic species is S-nitrosothiols (RSNOs), important biological nitric oxide carriers. In this contribution, we computationally demonstrate that protein environment can have a dramatic effect on the RSNO properties and reactivity by altering the antagonistic resonance structure balance. We argue that this precise and dynamic control may be one of the major factors determining the chemical biology of RSNOs. Through on-going collaborative efforts with experimentalists, evidence for enzymatic control of RSNO reactivity in physiologically-relevant reactions starts to emerge. Moreover, analysis of isoelectronic S-containing species suggests that the resonance structure antagonism is not unique to RSNOs, and may be relevant to protein control of several biologically important molecules.

*First-principles simulations of tribological processes*Nick Mosey

Queen's University

Friction and wear are ubiquitous phenomena that have significant environmental and economic impacts. For example, the annual costs associated with energy losses due to friction and the need to prematurely replace worn out equipment are estimated to be several percent of the GDP in industrialized nations. Furthermore, energy losses due to friction place additional demands on finite energy resources. In order to more effectively control friction and wear, it is necessary to have a better understanding of the processes that occur in sliding contacts. First-principles chemical simulation can play a key role in this respect, offering insight into the details of these processes at the atomic and electronic levels, and providing a means of characterizing the extreme conditions experienced in sliding contacts.

In this presentation, I will discuss our efforts to study lubricated sliding contacts through first-principles molecular dynamics simulation. Emphasis will be placed on two areas. First, I will discuss our recent exploration of sliding interfaces composed of hydroxylated surfaces. This work has shed light on how chemical interactions between sliding surfaces affect friction, and led to a predictive model that accounts for experimentally-observed deviations from Amontons' basic law of friction arising from these interactions. The development of such a model is a significant advancement in the basic understanding of friction. Second, I will discuss work aimed at using the extreme conditions experienced in sliding contacts to transform simple molecules into effective lubricants. Specifically, I will show how compression and shear can transform aldehydes into polyethers, which are known to be good lubricants. We suggest that reactions of this type could form the basis of a new approach to lubrication in which lubricant molecules actively adapt to the conditions experienced in contacts instead of merely acting as passive mechanical boundaries between sliding surfaces.

*Molecular dynamics simulations of ion transport
in G-quadruplex DNA Structures (ion channels)*

Parisa Akhshi and Gang Wu
Queen's University

Guanine-rich DNA sequences can form four-stranded structures called G-quadruplexes which play many important roles in various biological processes [1]. Although alkali metal ions such as sodium and potassium are critical for the stabilization of G-quadruplex structures, little is known about the ion dynamics in G-quadruplex DNA structures [2]. We have employed a combination of NMR spectroscopy and Molecular Dynamics (MD) simulations to study ion dynamics in G-quadruplex DNA and related structures. For the first time, we have performed Adaptive Biasing Force (ABF) [3,4] MD simulations to obtain Potential of Mean Force (PMF) profiles for ion movement inside G-quadruplex DNA channels. We have also compared ABF and Umbrella Sampling (US) results. These new MD simulations have provided new mechanistic insights into ion transport along G-quadruplex DNA channels.

[1] J. T. Davis, *Angew. Chem. Int. Ed.* **2004**, *43*, 668.

[2] P. Sket and J. Plavec, *J. Am. Chem. Soc.* **2010**, *132*, 12724.

[3] J. Hénin and C. Chipot, *J. Chem. Phys.* **2004**, *121*, 2904.

[4] C. Chipot and J. Hénin, *J. Chem. Phys.* **2005**, *123*, 244906.

Effective potential approach to the simulation of large para-hydrogen clusters and droplets

Mohammad Ashtari and Natalie Cann

Queen's University

Poly-L-proline chains have been shown[1-6] to function well as chiral stationary phases (CSPs) for enantiomeric resolution. However, the resolution mechanism of these CSPs has not yet been elucidated. To this end, molecular dynamics simulations (MD) of surface-bound polyprolines have been performed to study the interfacial structure, solvation and selectivity of these chiral interfaces. The simulated L-proline chains vary in length from dimers to hexamers, and the chains are terminated by either trimethylacetyl or t-butyl carbamate. These terminal groups are structurally quite similar but the former leads to a more selective interface [3]. Poly-L-proline chains exhibit a right- or left-handed helical structure depending on the polarity of the solvent. With this in mind, two solvents are examined in the simulations: a polar water/methanol and a relatively apolar n-hexane/2-propanol mixture. Selectivity simulations have been performed for a set of six enantiomers that are experimentally resolved on poly-L-proline CSPs. MD simulation results are compared with experimental data in which considerable differences are observed between various poly-L-proline stationary phases [2,3].

To capture the right energetic balance between the global minimum and other competing local minima and also to consider the energetics of conformational changes, extensive electronic structure calculations of each poly-L-proline have been performed. In particular, backbone amide dihedrals are examined with an analysis of coupling between dihedrals. Distinct force fields have been developed for each poly-L-proline.

[1] J. Huang, P. Zhang, H. Chen and T. Li, *Anal. Chem.* **2005**, 77, 3301.

[2] J. Huang, H.Chen and T. Li, *J. Chromatogr. A* **2006**, 1113, 109.

[3] J. Huang, H.Chen, P.Zhang nad T. Li, *J. Chromatogr. A* **2006**, 1109, 307.

[4] R. Sancho and C. Minguillon, *J. Chromatogr. B* **2008**, 875, 93.

[5] M. Li, J. Huang and T. Li, *J. Chromatogr. A* **2008**, 1191, 199.

[6] W. J. Lao and J. Gan, *J. Chromatogr. A* **2009**, 1216, 5020.

Antiferromagnetic ordering in the conjugated chains of disordered postpolymeric carbon: a case DFT investigation

Oleksiy Khavryuchenko

Kyiv National Taras Shevchenko University (Ukraine)

Establishing a comprehensive model of ACs and computing their properties is an intense area of research due to the wide application of carbon materials and their practical importance. However, the majority of such models are still based solely on ordered graphite-like clusters or non-bonded curved carbon sheets. Another aspect of the AC chemistry, which is often overlooked, is the dependence of the chemical and physical properties of the material under consideration on its spin state (i.e. multiplicity). In this work, we report and discuss the results of density-functional theory calculations of the electronic structure and spin properties of both graphite-like and disordered carbon clusters, as models of the postulated two major domains of AC.

Spatial structure of the amorphous domain cluster has been constructed from a series of different polymer-precursors models by simulation of carbonization through stepwise elimination of hydrogens and subsequent optimization of the geometry in different multiplicity states. The final geometry, being unique, is taken as an arbitrary model for a disordered amorphous domain as the one, representing typical statistic distribution of properties.

*Evaporation and condensation of small charged
clusters of water and methanol*

Christopher Daub and Natalie Cann
Queen's University

We are studying small clusters (up to 40 molecules) of water and/or methanol containing a single sodium, calcium, chloride or iodide ion with polarizable potential models and classical MD. We examine evaporation and condensation events over long simulation times, both in vacuum and in argon gas at atmospheric pressure. Simulations at different initial cluster and/or gas temperatures allow us to examine the entire range of possible cluster sizes down to bare ions. Our findings give insight into the behaviour of ions at interfaces and the mechanisms of solvent loss from charged clusters in electrosprays.

Investigation of ionic cluster hydration with the newly parameterized self-consistent charge density-functional tight binding model

Vibin Thomas, Ugo Rivard, and Radu Iftimie

Université de Montréal

Bimolecular proton transfer in solution is the simplest and extremely important class of charge transfer reactions. These reactions are known to occur in two steps. In the first step diffusive motion of the reactant species leads to the formation of a sterically favourable ‘encounter complex’. In the second step, charge-transfer occurs inside the encounter complex at some intrinsic rate. Since the intrinsic rate for proton transfer is often extremely high in aqueous solution, the overall rates of such reactions tend to be ‘diffusion limited’ or ‘diffusion influenced’. As a result, experimental access to the reaction kinetics inside the encounter complex has proven to be rather difficult. However, recent investigations using ultrafast pump-probe spectroscopy (both visible and infrared) to study bimolecular excited-state proton transfer at high base/acceptor concentration have yielded new insights on the proton transfer mechanisms involved inside solvent-separated encounter complexes. Unfortunately there are rather significant limitations on information that these ensemble measurements can provide. Specific, model independent details on the nature of the charge transfer mechanism, their diversity and distribution are difficult to extract from the experimental data alone, which tends to measure the time-dependent population of reactants/products and intermediates averaged over the whole probe volume. It is currently not feasible to study bimolecular proton transfer in solution at the ‘single-molecule’ level and ultrafast timescale.

Given the current limitations of experiment, we have developed a first-principles molecular dynamics approach to study the mechanisms involved in aqueous intermolecular proton transfer in solvent-separated encounter complexes. In particular, the goal of this work was to provide detailed atomistic information on the proton transfer reaction dynamics when a single water molecule bridges the donor and acceptor sites of the reactants in solution and hence to supplement the experimental studies.

This presentation is focussed on the distinct proton transfer pathways which contribute to acid-base neutralization reactions inside solvent-separated encounter complexes between a phenolic and carboxylic molecules. The nature of the various pathways observed is also discussed in context of previous experimental works along with the computed time resolved vibrational spectra utilizing complex Morlet wavelet transforms.

Posters

***Structural and thermodynamic characterization
of the first oligomeric structures of Human Amylin
using Coarse-grained Replica Exchange Molecular Dynamics simulations***

Saïd Bouzakraoui and Normand Mousseau
Université de Montréal

Amyloid formation plays a key role in a wide range of diseases including Alzheimer's disease, Parkinson's disease, and Huntington's disease [1,2]. Human islet amyloid polypeptide (amylin, hIAPP) is a 37 residue polypeptide, which is the major component of the pancreatic islet amyloid associated with type 2 diabetes and is one of the most amyloidogenic polypeptides known [3]. Although a structure of hIAPP fibrils has been obtained, structures of early oligomers and mechanism of β -sheet formation remain poorly understood peptide [4]. Further, early oligomers have been involved as the primary cytotoxic components of the aggregation pathway [5]. Thus, characterizing the structures of early hIAPP oligomers is critical for a better understanding of the aggregation process.

In this study, following our previous numerical work on the structure of the monomer and dimer of full-length IAPP [6], we characterize the atomic structure and the thermodynamics of the 14-37 residue hIAPP fragment using Replica exchange molecular dynamics (REMD) coupled with OPEP coarse-grained protein force field [7]. Wild-type and mutated monomers, dimers and trimer are studied to identify key elements of the aggregation process [8,9].

- [1] J.D. Sipe, *Crit. Rev. Clin. Lab. Sci.* **1994**, *31*, 325-354.
- [2] D. Selkoe, *J. Nat. Cell. Biol.* **2004**, *6*, 1054-1061.
- [3] J.W. Happener, C. Lips and J. Int. *J. Biochem. Cell Biol.* **2006**, *38*, 726.
- [4] S. Luca, W.M. Yau, R. Leapman and R. Tycko, *Biochemistry* **2007**, *46*, 13505.
- [5] C.Y. Lin, T. Gurlo, R. Kaye, A.E. Butler, L. Haataja, C.G. Glabe and P. C. Butler, *Diabetes* **2007**, *56*, 1324.
- [6] R. Laghaei, N. Mousseau and G. Wei, *J. Phys. Chem. B*, **2011**, *115*, 3146.
- [7] J. Maupetit, P. Tuffery and P. Derreumaux, *Proteins: Struct. Funct. Bioinf.* **2007**, *69*, 394.
- [8] L. Wei, P. Jiang, W. Xu, H. Li, H. Zhang, L. Yan, M.B. Chan-Park, X.W. Liu, K. Tang, Y. Mu and K. Pervushin, *J. Biol. Chem.*, **2011**, *286*, 6291.
- [9] K.E. Marshall, K.L. Morris, D. Charlton, N. O'Reilly, L. Lewis, H. Walden and L.C. Serpell, *Biochemistry*, **2011**, *50*, 2061.

***Long-Distance Sulfate-Patterning of Water:
Spectral Signature and Structure***

Xijun Wang, Soran Jahangiri, and Gilles Peslherbe
Concordia University

Sulfate ions are believed to be *water structure-making* species because they would *pattern* water around it to form a hydration shell structure, but no clear consensus has been reached as to what extent can sulfate ions structure the water. A recent experimental study based on infrared photodissociation (IRPD) spectroscopy suggests that sulfate-water clusters can be used as appropriate models to investigate the effects of anions on water structure, and that the OH stretching frequency of the surface water molecules could be taken as a signature of the hydration distance (O'Brien, Prell, Bush, and Williams, *J. Am. Chem. Soc.* 2010). In this contribution, we address these issues and proposals computationally with molecular dynamics simulations. The infrared spectra of sulfate-water clusters of varying size are calculated from the Fourier Transform of the autocorrelation function of the total dipole moment of the cluster, and the interatomic interactions are described by the self-consistent-charge density-functional tight-binding (SCC-DFTB) model. The experimental signature of these clusters is well reproduced, which brings confidence in the results and encourages further structural analysis to complement and augment experimental data on ion hydration.

Poster 3

Accounting for polarization in molecular wires with self-consistent Huckel theory

Randall Dumont
McMaster University

Conduction through molecular wires is simulated using the source-sink potential method of Goyer, Ernzerhof and Zhuang [*J. Chem. Phys.* **2007**, *126*, 144104], implemented using simple self-consistent Huckel theory in order to account for polarization effects resulting from potential bias.

Computational study of weak interactions in the stabilization of unfavourable tert-butyl substituted cyclohexane conformers

Philippe Archambault and Heidi Muchall

Concordia University

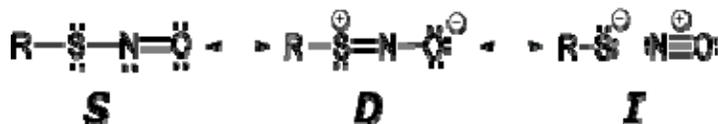
The free energy difference, ΔG° , between axial and equatorial substituted cyclohexanes is called the A-value. The bulky tert-butyl group has the highest A-value of about 20 kJ/mol. This translates to a population density of over 99% for the equatorial conformer where such a high ratio (3:10⁻⁴:1) anchors the ring conformation. This study used substituents with potential transannular weak interactions, such as lithium...halogen and hydroxyl...halogen, to stabilize the chair conformation with the tert-butyl group in the axial position. Both types of interactions resulted in a substantial preference for axial substitution.

Ground-state properties of LiH by Reptation Quantum Monte Carlo

Matthew Flister, Marat Talipov, and Qadir Timerghazin
Marquette University

S-Nitrosothiols are known to be important in the storage and transport of nitric oxide NO in biological systems. Recently, it has been shown that the electronic structure of RSNOs can be described by a combination of three resonance structures: conventional structure, zwitterionic, and ion pair (see scheme).

Two of these resonance structures, zwitterionic and ion pair, suggest very different bonding patterns and charge distribution. It can be expected that the nature of the substituent R should affect the relative contributions of these resonance structures and therefore effectively modulate the chemical properties of RSNOs. In this contribution, we present a computational study of the substituent effects in model RSNOs and correlate them against known empirical parameters for substituents R. Various properties of RSNOs will be examined, including bond dissociation energies and cis-trans isomerization barriers. Electronic structure of the SNO group will be discussed using Natural Bond Orbital (NBO) approach. We will show correlations for several parameters and discuss the field-inductive effects of substituents on RSNO structure and reactivity.



Electrogenic transport mechanisms in ammonium transporters

Shihao Wang and Guillaume Lamoureux
Concordia University

Proteins of the Amt family have an important role in ammonium transport, especially at low external ammonium concentrations. Some members of the family are known to facilitate the diffusion of the neutral NH_3 , while others transport the positively charged NH_4^+ . However, mechanistic investigations of the permeation mechanism published so far focus on the diffusion of NH_3 , while the NH_4^+ ion transport mechanism is still unclear. We have used state-of-the-art computational techniques to investigate the NH_4^+ transport process in *Escherichia coli*'s AmtB, and have uncovered a new transport mechanism. In this mechanism, NH_4^+ first passes a gate that is formed by two phenyl rings, and then split itself into two fragments, which are transported separately: NH_3 , through a hydrophobic pore, and H^+ , through a pair of highly conserved histidine residues. The two fragments are recombined at the lower end of the pore to form NH_4^+ again. This mechanism is applicable to other members of the Amt/MEP/Rh family because the amino acid composition along the pore is highly conserved.

Computational Investigation of the Hydration of Alkyl Diammonium Chlorides and their Effect on Water/Organic Phase Separation

Soran Jahangiri, Sean Mercer, Philip Jessop, and Gilles Peslherbe
Concordia University

The hydration of alkyl diammonium chlorides of varying alkyl chain length and their effect on the solvation of small organic molecules has been investigated by molecular dynamics (MD) simulations. Water-tetrahydrofuran and water-acetonitrile liquid mixtures containing alkyl diammonium chlorides with aliphatic chains of 2, 4, 6 and 8 carbon atoms were simulated in order to investigate the effect of the diammonium carbon chain length on the salting-out of organic molecules. Potential of mean force (PMF) calculations and structural analyses of the MD trajectories were carried out to characterize these effects, unveiling the specific effect of diammonium chlorides on salting organic molecules out of the aqueous phase. The strength of the hydrophobic interactions between diammonium dications and organic solutes was found to be a key factor in understanding the underlying mechanism of the specific effect.

***Charge-Transfer-to-Solvent Dynamics in
Photoexcited Iodide-Methanol Clusters***

Chun Chi Mak and Gilles Peslherbe
Concordia University

The solvated electron, a ubiquitous but mysterious species in polar liquids such as water and alcohols, is believed to be a key intermediate in various synthetically important reactions in organic chemistry. Iodide-polar solvent clusters photoexcited to the charge-transfer-to-solvent (CTTS) state provide an important paradigm for investigating the molecular details of the solvated electron, and recently, femtosecond photoelectron spectroscopy has been used to probe the dynamics of CTTS excited $\Gamma(\text{CH}_3\text{OH})_n$ ($n=4-11$) [Young, Yandell and Neumark, *J. Chem. Phys.* 2011]. These experiments suggest that the excited electron in small CTTS excited $\Gamma(\text{CH}_3\text{OH})_n$ ($n=4-11$) undergoes autodetachment after being trapped briefly by the $\text{I}\cdots(\text{CH}_3\text{OH})_n$ network, since small methanol clusters, unlike larger methanol clusters or liquid methanol, are not able to efficiently solvate excess electrons.

In this contribution, computer simulations are used to unveil the mechanism of relaxation and decay of CTTS excited $\Gamma(\text{CH}_3\text{OH})_n$. Ground-state geometries of small $\Gamma(\text{CH}_3\text{OH})_n$ ($n=2-5$) are first characterised to understand the key features of halide solvation in small methanol clusters. Excited-state *ab initio* molecular dynamics simulations of CTTS $\Gamma(\text{CH}_3\text{OH})_n$ are then performed. Preliminary simulation results for small $\Gamma(\text{CH}_3\text{OH})_n$ ($n=2,3$) suggest that the dynamics of CTTS excited $\Gamma(\text{CH}_3\text{OH})_n$ is characterised by a complex interplay between iodine-methanol, electron-methanol and methanol-methanol interactions. These same interactions may play a pivotal role in determining the properties of the solvated electron in alcohols.

List of Participants

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Ian Hamilton	Wilfrid Laurier University
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Nick Mosey	Queen's University
Heidi Muchall	Concordia University
Esam Orabi	Concordia University
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