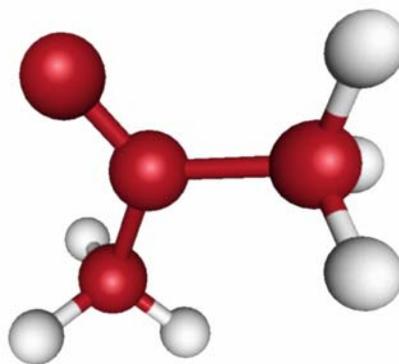
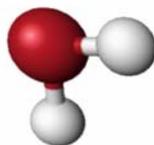




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CERMM

Centre for Research in Molecular Modeling
Centre de Recherche en Modélisation Moléculaire

The Fourth Annual Symposium

Richard J. Renaud Science Complex, Concordia University

7141 Sherbrooke Street West, Montréal

Friday, March 26, and Saturday, March 27, 2004

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FOR HELP WITH ORGANIZATION

SYMPOSIUM PROGRAM

Friday, March 26, PM, Room SP-S-110

Chair: Dongqing Wei (Tianjin Normal University)

02:00 Opening address – Gilles Peslherbe

02:15 Plenary lecture - Ray Kapral (University of Toronto)

It Takes Only a Skip, Hop and a Jump to Find Quantum Reaction Rates in Classical Solvents

03:15 Coffee break

03:45 Sichuan Xu (Ecole Normale Supérieure), Celine Toubin (PhLAM-USTL Lille1, Lille, France), Gilles H. Peslherbe (Concordia University), and Casey Hynes (Ecole Normale Supérieure/University of Colorado)

A Model Study of a Key Step in the Strecker Route to Glycine Formation in the Interstellar Medium

04:15 Andrew Ryzhkov and Parisa Ariya (McGill University)

A Density functional study of complexes and reactions of benzene and toluene with chlorine atoms

04:35 Scott Bohle (McGill University)

Theory aided synthesis of nitric oxide adducts

04:55 Qadir Timerghazin and Gilles Peslherbe (Concordia University)

Topological Approach to the Solvated and Dipole-Bound Electron

05:15 Tao-Nhân Nguyen, Gilles Peslherbe (Concordia University) and Holger Vach (Ecole Polytechnique, Paris)

Novel Oxidation Process of a Si(100) Surface by (O₂)_n Clusters

05:35 Byung Chan Eu and Kyunil Rah (McGill University)

Viscosity and Self-Diffusion Coefficients of Supercooled Liquids

06:05 End of session

07:30 Symposium Banquet – *Le Caveau*, 2036 Victoria Street

Saturday, March 27, AM, Room SP-S-110

Chair: Tucker Carrington (Université de Montréal)

09:00 Jeremy Schofield (University of Toronto) and Radu Iftimie (NYU)

Efficient ab-initio simulation of proton transfer reactions in simple and condensed phases: Implications for molecular modeling

09:30 Xiaogang Wang and Tucker Carrington (Université de Montréal)

Contracted Basis Lanczos Methods for Computing Numerically Exact Rovibrational Levels of Methane

09:50 Richard Dawes and Tucker Carrington (Université de Montréal)

A multidimensional discrete variable representation basis obtained by simultaneous diagonalization

10:10 **Jamal Dawoud, A. Sallabi, and David Jack (Concordia University)**

Structures of hydrogen adsorbed on MgO and NaCl

10:30 Coffee break

Saturday, March 27, AM, Room SP-S-110

Chair: Régis Pomès (University of Toronto)

11:00 **Patrick Lagüe (Université Laval)**

Protein-Membrane and Membrane-Mediated Protein-Protein Interactions Studied by Integral Equations

11:30 **Maria Sabaye Moghaddam, (University of Toronto), Seishi Shimizu (University of York), and Hue Sun Chan (University of Toronto)**

A Monte Carlo Study of Temperature Dependence of Three-Body Hydrophobic Interactions

11:50 **Sean Hughes, Tao-Nhân Nguyen and Gilles Peslherbe (Concordia University)**

New Model for Predicting Structural and Thermodynamic Properties of Ln³⁺ Water Clusters

12:10 **Christian Reber (Université de Montréal)**

Electronic structure of transition metal complexes - spectroscopy and computational modeling

12:30 Lunch – Poster Presentation session

Saturday, March 27, PM, Room SP-S-110

Chair: Heidi Muchall (Concordia University)

03:00 **Nicolas Moitessier (McGill University)**

Toward a Computational Tool Predicting the Stereochemical Outcome of Asymmetric Reactions

03:30 **Paul Loncke and Gilles Peslherbe (Concordia University)**

Mechanisms of Intramolecular Rearrangements of Cyclic Siloxycarbenes

03:50 **Robert Mawhinney, Heidi Muchall, and Gilles Peslherbe (Concordia University)**

Deducing the Electronic Structure of Nitrilimine

04:10 **Lei Zhang, Heidi Muchall, and Gilles Peslherbe (Concordia University)**

Calculation and Assignment of Absorption Spectra of Phenol Radical Cations: 580 nm Absorption of the 3,5-Dimethoxyphenol Radical Cation

04:30 **Roger Gaudreault, Tony Whitehead, and T.G.M.van de Ven (McGill University)**

Mechanisms of Flocculation with Poly(ethylene oxide) and Novel Cofactors: Theory and Experiment

04:50 **Cecile Malardier-Jugroot, T.G.M.van de Ven, and Tony Whitehead (McGill University)**

Characterisation of a novel self-association of an alternating copolymer into nanotubes in solution

05:10 **Tony Whitehead (McGill University), Adam Dickie (NRC Laboratory, Edmonton, Alberta), Felaniaina Rakotondradany (University of Alberta), Asok Kakkar and Hanadi Sleiman (McGill University)**

Theoretical Predictions and Experimental Realizations: self assembling tin-alkynyl molecules on silica surfaces and hydrogen bonded rosettes of dinitobenzoic acid

05:40 Closing

POSTER PRESENTATIONS

- 1 **Denise M. Koch, Qadir K. Timerghazin, Gilles H. Peslherbe (Concordia University), Branka M. Ladanyi (Colorado State University), and James T. Hynes, (Ecole Normale Supérieure and University of Colorado)**
Spectroscopy of $\text{NaI}(\text{H}_2\text{O})_n$ Clusters
- 2 **Grygoriy Dolgonos (Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland and Concordia University)**
How many hydrogen molecules can be inserted into C_{60} ?
- 3 **Pratibha Malla and Heidi Muchall (Concordia University)**
*Computational Studies of *N*-phenyl-*N*'-sulfinylhydrazines: Factors Influencing Dimerization*
- 4 **Elena Ivanova and Heidi Muchall (Concordia University)**
*Computational study of complex formation and reaction of *N*-sulfinylamines with water*
- 5 **Svetlana Popenova, Philippe Merle and Gilles Peslherbe (Concordia University)**
Computational studies of intramolecular agostic ancillary ligand - metal interactions in cationic zirconocenium complexes
- 6 **Sacha Zlatkova (Concordia University) and Zorka Smedarchina (NRC)**
Theoretical Study of Tunnelling in Proton Transfer Laser Dyes: The 2-(2'-Hydroxyphenyl)Benzimidazole as a Test Case
- 7 **Yin Wei and Gilles Peslherbe (Concordia University)**
Computational Studies of the Reactivity of Vanadium Oxide Clusters towards Halocarbons
- 8 **Etienne Paradis (Concordia University) and Alain St-Amant (University of Ottawa)**
Implementation of functionality QM/MM in DeFT and application to calculations of the free energy
- 9 **Jean Christophe Tremblay and Tucker Carrington Jr. (Université de Montréal)**
A Preconditioned Iterative Method for Studying the Acetylene/Vinylidene Isomerization
- 10 **Mouna Sbata and Joël Schamps (Université des Sciences et Technologies de Lille)**
Electronic structure and radiative lifetimes of the LaF^+ radical
- 11 **Mouna Sbata and Gilles Peslherbe (Concordia University)**
Quantum Monte Carlo Simulations of $\text{I}(\text{H}_2\text{O})_n$ and $\text{Na}^+(\text{H}_2\text{O})_n$ ($n=12, 20$) clusters ($n=12, 20$)
- 12 **X. F. Wang, P. Vasilopoulos (Concordia University) and F. Peeters (Universiteit Antwerpen)**
Spin-dependent transmission through periodically stubbed waveguides due to spin-orbit interaction: influence of subband mixing
- 13 **Sichuan Xu, Gilles Peslherbe (Concordia University), and James T. Hynes (Ecole Normale Supérieure and University of Colorado)**
Theoretical Study of the Mechanism of Aminoacetonitrile Hydrolysis

Plenary Lecture

Friday, 2:15–3:15 PM

**It Takes Only a Skip, Hop and a Jump to Find
Quantum Reaction Rates in Classical Solvents**

Raymond Kapral (Dept. of Chemistry, University of Toronto)

Many reactions are quantum mechanical in nature and cannot be approximated adequately using classical mechanics. For instance, proton and electron transfer reactions are ubiquitous in chemical and biochemical systems and the calculations of their rates and the elucidation of their mechanisms in the condensed phase present challenges for simulation. Since it is impossible to treat the entire condensed phase system quantum mechanically, it is natural to account for the quantum nature of the proton or electron but use classical mechanics to describe the solvent. However, quantum mechanics and classical mechanics are like oil and water: they don't like to mix. In spite of this reluctance to mix, we show how these descriptions can be combined to study quantum reaction rates in the condensed phase at a microscopic level.

Oral Presentation

Friday, 3:45–4:15 PM

**A Model Study of a Key Step in the Strecker Route to
Glycine Formation in the Interstellar Medium**

Sichuan Xu (Ecole Normale Supérieure, Paris, France),

Celine Toubin (PhLAM-USTL Lille1, Lille, France),

Gilles H. Peslherbe (CERMM and Dept. of Chemistry & Biochemistry, Concordia University),

James T. Hynes (Ecole Normale Supérieure, Paris, France; University of Colorado at Boulder)

The amino acid glycine has recently been detected in the interstellar medium (ISM). Here we present the results of a theoretical study of a key step of a possible Strecker synthesis route to glycine occurring at the surface of icy grain mantles ($T \approx 30\text{--}50\text{K}$) in the ISM. In particular, we focus on the reaction between methylene imine (CH_2NH) and hydrogen cyanide isomers (HCN or HNC) to produce aminoacetonitrile (H_2CNNH_2), which in a subsequent hydrolysis step would produce glycine. Electronic structure calculations indicate that this reaction can proceed with a very low barrier $\approx 1\text{kcal/mol}$ with the isomer HNC , but with a much higher and prohibitive barrier for reaction with HCN . The mechanism is found to involve a proton transfer chain via water molecules in the surface region.

Oral Presentation

Friday, 4:15–4:35 PM

A Density Functional Study of Complexes and Reactions of Benzene and Toluene with Chlorine Atoms

Andrew B. Ryzhkoy, (Dept. of Atmospheric and Oceanic Sciences, McGill University) and Parisa A. Ariya, (Dept. of Chemistry, and Dept. of Atmospheric and Oceanic Sciences, McGill University)

Aromatic compounds such as benzene, toluene, and xylene present a large portion of the volatile organic compounds (VOC) in urban areas. These compounds can have a direct effect on human health as well as contribute to the formation of secondary air pollutants, including ozone. The main oxidation and degradation way of aromatic compounds is supposed to be the reaction with OH radicals. However, it has been suggested that Cl atoms may play a significant role in the loss process of these species. In present work, we have studied complexes and reactions of benzene and toluene using modern hybrid functional PBE1PBE method with the 6-311+G** basis set. Three stationary structures have been found for PhH...Cl complex: hexahapto-complex, π -complex and σ -complex. The first one is first order saddle point and so it is not stable. Potential energy surface scan proves this point and shows that it is a transition state between two equivalent π -complexes. PhMe...Cl has additional structures due to ipso-, ortho-, meta- and para-isomerization. The stability of all complexes found was calculated and compared. Two pathways of reaction of benzene and toluene with Cl atom were found: the hydrogen abstraction reaction by Cl atom, which is found to be barrierless endothermic, and the hydrogen substitution reaction, which in contrast has relatively high energy of activation.

Oral Presentation

Friday, 4:35–4:55 PM

Theory Aided Synthesis of Nitric Oxide Adducts

Scott Bohle (Dept. of Chemistry, McGill University)

Theoretical calculations, especially density functional calculations with large basis sets, are critical for our research into the reactions of organic derivatives with nitric oxide. For example, with alcohols and ketones the products can vary enormously and range from simple {N(O)=NO} fragments from the addition of two nitric oxides to more complicated structures corresponding to the addition of six NOs. Identifying these products can be very difficult and often requires X-ray crystallography. However we have found instead that trial structures and possible products can be readily optimized and their frequencies calculated by modern ab initio methods. These vibrational frequencies, and their predicted isotopic shifts, are invaluable for product determination and it is gratifying how well the B3LYP/6-311++G** level works for these electron rich compounds. Have we reached the age where theory really can guide experiment?

Oral Presentation

Friday, 4:55–5:15 PM

Topological Approach to the Solvated and Dipole-Bound Electron

Qadir K. Timerghazin and Gilles H. Peslherbe

(CERMM and Dept. of Chemistry & Biochemistry, Concordia University)

An electron can interact with a cluster of polar neutral mols. in two ways: it can either reside outside the cluster, trapped in the field of the cluster dipole moment (dipole-bound electron), or inside the cluster (solvated electron). Studies of both species are of great importance to further our understanding of the bulk solvated electron phenomenon and, from a more general perspective, the interaction of electrons with molecules. In this work we will present the topological approach to the analysis of the electron density distribution in the cluster anions with dipole-bound or solvated electron with the Atoms-In-Molecule (AIM) theory approach. Generic topological patterns by which the dipole-bound or solvated electron manifests itself in polar solvent cluster anions will be presented, and numerical parameters to characterize the nature of electron binding will be proposed.

Oral Presentation

Friday, 5:15–5:35 PM

Novel Oxidation Process of a Si(100) Surface by $(\text{O}_2)_n$ Clusters

Tao-Nhân V. Nguyen and Gilles H. Peslherbe (CERMM and Dept. of Chemistry & Biochemistry, Concordia University) and Holger Vach (Laboratoire de Physique des Interfaces et des Couches Minces CNRS, Ecole Polytechnique, Paris, France)

Recent experimental results show evidence for a completely new oxidation process of silicon surfaces with an $(\text{O}_2)_m$ cluster beam [1]. It was postulated that the reaction is cluster-catalyzed and proceeds via molecular oxygen dissociation, akin to processes observed in the famous “burning of air” [2]. This interpretation has been tested by a theoretical study of $(\text{N}_2)_m$ and $(\text{O}_2)_m$ surface scattering. When simulating the collision at experimental conditions, the cluster products are only slightly vibrationally excited and molecular dissociation is not possible. Surprisingly, the cluster size does not catalyze but hinders monomer vibrational excitation, suggesting the existence of an optimal cluster size for cluster-catalyzed reactions. Alternatively, the possibility of direct surface oxidation by molecular oxygen is investigated. However, a study of the molecular properties in the course of the surface collision showed that the molecules can not be excited enough to allow for the molecular oxidation channel to occur. An alternate reaction path is proposed to explain the experimental findings.

[1] D. V. Daineka *et al.*, J. Appl. Phys. 92, 1 (2002).

[2] T. Raz *et al.*, Chem. Phys. Lett., 246, 405, (1995).

Oral Presentation

Friday, 5:35–6:05 PM

Viscosity and Self-Diffusion Coefficients of Supercooled Liquids

Byung Chan Eu (Dept. of Chemistry and RQMP, McGill University) and Kyunil Rah (Dept. of Chemistry, McGill University)

A theory of viscosity and self-diffusion coefficients of supercooled liquids will be presented and applied to study the temperature dependence of viscosity and self-diffusion coefficients of supercooled liquids down to the glass transition temperature. The strong and fragile liquids are examined and the theory compares excellently with experiment.

K. Rah and B. C. Eu, Phys. Rev. E 68, 051204 (2003).

K. Rah and B. C. Eu, Phys. Rev. E (submitted).

K. Rah and B. C. Eu, Phys. Rev. E (submitted).

Oral Presentation

Saturday, 9:00–9:30 AM

Efficient *Ab-Initio* Simulation of Proton Transfer Reactions in Simple and Condensed Phases: Implications for Molecular Modeling

Jeremy Schofield, (Chemical Physics Theory Group, University of Toronto) and Radu Iftimie (NYU)

An efficient method for sampling the relevant state space in simple and condensed phase proton transfer reactions is proposed. In the present method, the reaction is described by solving the electronic Schrödinger equation for the reaction centre in the presence of explicit solvent molecules whose interactions are described via molecular mechanics potentials. The sampling algorithm uses a molecular mechanics guiding potential in combination with simulated tempering ideas and allows thorough exploration of the reactive state space in the context of an ab initio calculation even when the dielectric relaxation time is long. The method is applied to investigate the connection between kinetic isotope effects and reaction mechanism in model proton transfer processes. Our studies suggest that care should be exercised in the construction of molecular mechanics potentials to describe bond-breaking and bond-forming events since small differences in functional form can induce artefacts in the calculated secondary kinetic isotope effects. In particular, we demonstrate that empirical valence bond potentials commonly used in classical descriptions of chemical processes can lead to secondary kinetic isotope effects which disagree with those observed in accurate ab-initio simulations.

Oral Presentation

Saturday, 9:30–9:50 AM

Contracted Basis Lanczos Methods for Computing Numerically Exact Rovibrational Levels of Methane

X.-G. Wang and T. Carrington, Jr. (Département de chimie, Université de Montréal)

We present the first numerically exact calculation of rovibrational levels of a five-atom molecule, extending the method we used for calculating vibrational levels of the same molecule [X.-G. Wang, T. Carrington, Jr, J. Chem. Phys. 118, 6946 (2003) and 119, 101 (2003)]. Two contracted basis Lanczos strategies are proposed. The first and preferred strategy is a two-stage contraction. Products of eigenfunctions of a 4D stretch problem and eigenfunctions of 5D bend-rotation problems, one for each K , are used as basis functions for computing eigenfunctions and eigenvalues (for each K) of the Hamiltonian without the Coriolis coupling term. Finally, energy levels of the full Hamiltonian are calculated in a basis of the eigenfunctions of the Hamiltonian without the Coriolis coupling term. The second strategy is a one-stage contraction in which energy levels of the full Hamiltonian are computed in the product contracted basis (without first computing eigenfunctions of the Hamiltonian without the Coriolis coupling term). The two-stage contraction strategy, albeit more complicated, has the crucial advantage that it is trivial to parallelize the calculation so that the CPU and memory costs are independent of J . We use the polar coordinates associated with orthogonal Radau vectors and spherical harmonic type rovibrational basis functions. A new parity-adapted rovibrational basis suitable for a five-atom molecule is proposed and employed to obtain bend-rotation eigenfunctions in the first step of both contraction methods. The effectiveness of the two methods is demonstrated by calculating a large number of converged $J=1$ rovibrational levels of methane (up to 8000 cm^{-1}) using a global potential energy surface. We also present the use of C_{3v} invariant quadrature grid to implement the C_{3v} symmetry in computing rovibrational levels of methane.

Oral Presentation

Saturday, 9:50–10:10 AM

A Multidimensional Discrete Variable Representation Basis Obtained by Simultaneous Diagonalization

Richard Dawes and Tucker Carrington Jr. (Département de chimie, Université de Montréal)

A multidimensional DVR basis set is usually constructed as a direct product of 1D DVRs. Although restrictive and inefficient (large numbers of functions are required), direct product bases are advantageous computationally. In particular, the coordinate operator is diagonal, leading to trivial evaluation of the potential energy contribution to Hamiltonian matrix-vector products. We discuss how an efficient (smaller) non-product basis may be constructed in two or more dimensions retaining maximal diagonality of the coordinate representations, and thus a potential that is approximately diagonal. Eigenvalues are then computed using this approximation. The effectiveness of this method is evaluated for some model 4D problems. The 4D basis is a product of two 2D DVR basis sets, each of which is obtained from a 2D basis of eigenfunctions of a 2D subproblem. Results will be discussed for stretch type problems such as coupled Morse oscillators and skewed multi-well potentials, as well as for bend problems using a basis of spherical harmonic functions. The success of this approach could allow theorists to compute spectra, rate constants etc, for systems beyond the reach of conventional methods.

Oral Presentation

Saturday, 10:10–10:30 AM

Structures of Hydrogen Adsorbed on MgO and NaCl

J. N. Dawoud, A. K. Sallabi, and D. B. Jack

(Dept. of Chemistry & Biochemistry, Concordia University)

The structure of adsorbed layers of hydrogen on MgO and NaCl substrates have been investigated using the Metropolis Monte Carlo method. In agreement with experimental work, it was found that hydrogen molecules on MgO arrange themselves in sequence of coverage dependent structures, namely, (2x2), (4x2), and (6x2) phases. Subsequent calculations using perturbation theory shows that these phases consist of "ortho state" molecules in the "helicoptering" rotational state, that lie flat on the surface, and "cartwheeling" rotational state. For the NaCl substrate the molecules occupy all of the Na⁺ sites in the "helicoptering" state. Additional molecules form a second layer with the molecules localised near the Cl⁻ sites in mixed states.

Oral Presentation

Saturday, 11:00–11:30 AM

Protein-Membrane and Membrane-Mediated Protein-Protein Interactions Studied by Integral Equations

Patrick Lagüe

*(Centre de Recherche sur la Fonction, la Structure, l'Ingénierie des Protéines,
Université Laval)*

Benoît Roux (Weill Medical College of Cornell University, New-York)

Proteins and cell membranes are playing key roles in the life process. The protein-membrane and membrane-mediated protein-protein interactions are investigated with 3D Hypernetted Chain (HNC) integral equations. These equations are derived from the statistical mechanical theory of liquids, and describe the perturbation on a nonuniform system, such as a membrane bilayer, arising from nonelectrostatic interactions with an embedded protein. The nonuniform distribution function of the atoms of the unperturbed system is required. This distribution function is extracted from a detailed molecular dynamics simulation of a pure DPPC bilayer with surrounding bulk waters. The peptide used in this study is modeled as a hard repulsive cylinder with a radius of 5 Å and a length of 37 Å; these dimensions correspond to those of a 25 residus α -helix of poly-alanine. The average membrane perturbation around the peptide, as well as the membrane-mediated peptide-peptide interactions, are presented.

Oral Presentation

Saturday, 11:30–11:50 PM

A Monte Carlo Study of Temperature Dependence of Three-Body Hydrophobic Interactions

Maria Sabaye Moghaddam, (Dept. of Biochemistry, University of Toronto),

Seishi Shimizu (Dept. of Biochemistry, The University of York)

Hue Sun Chan (Dept. of Biochemistry, University of Toronto)

More than forty years ago, Kauzmann hypothesized that hydrophobicity was the dominant driving force in protein folding. Studies of small nonpolar solutes in water as a model system to study the hydrophobic effect on protein denaturation have flourished over the last decade. In one of the most common approaches, the change in solvent accessible surface area (SASA) of hydrophobic solutes upon hydration is related to the change in thermodynamic properties of the system such as free energy or heat capacity. There is a basic assumption of additivity in this type of approach. That is, it is assumed that the methods used in small single solute experiments can be simply generalized to very large molecules such as proteins. The practical application of this assumption is achieved by addition of surface area of individual amino acids and relating it to the free energy or heat capacity of the whole protein. In this work, association of three methane-like solutes in water are studied by Monte Carlo simulations at various temperatures. Thermodynamic properties such as free energy and heat capacity are computed and compared with SASA predictions. Free energy and heat capacity seem to be dependent on the intersolute separation in a nonmonotonic way contrary to SASA predictions. We have also tested the assumption of pairwise additivity, the validity of which changes with temperature and intersolute separation.

Oral Presentation

Saturday, 11:50–12:10 AM

A New Model for Predicting Structural and Thermodynamic Properties of Ln³⁺ Water Clusters

S.R. Hughes, T.-N. Nguyen, J. A. Capobianco, G.H. Peslherbe
(CERMM and Dept. of Chemistry and Biochemistry, Concordia University)

In this study, we present improvements to models previously developed by our group to characterize the microsolvation of lanthanide metal ions in clusters. These models have been parameterized to high-level, ab initio calculations of small Ln³⁺-water dimers and include Coulombic, polarization and repulsion-dispersion terms. Clusters of the form [M(H₂O)_n]³⁺ have been studied for their structural and thermodynamic properties for sizes n={1,128}. Our results indicate that the coordination number of the Ln³⁺ ion within the first coordination shell is cluster-size dependent. In addition, the effects of lanthanide contraction on coordination and site symmetry are reproduced in our simulations. We have also predicted several energetic properties, including the stepwise binding energies, which have yet to be measured experimentally. Furthermore, the convergence of thermodynamic properties to bulk-like values is achieved at cluster sizes n>64, thus demonstrating the long-range influence of Ln³⁺ on the surrounding solvent.

Oral Presentation

Saturday, 12:10–12:30 PM

Electronic Structure of Transition Metal Complexes – Spectroscopy and Computational Modeling

Christian Reber (Département de chimie, Université de Montréal)

Their rich variety of electronic states makes transition metal compounds ideal models to study detailed electronic structure by both experimental spectroscopic and computational modeling methodologies. The resulting insight is of relevance for both understanding (photo)chemical reactivities and applications as optical materials.(1) Two fundamental case studies using compounds with symmetry-related sequences of electronic states will be presented. First, the interactions between electronic states in the octahedral hexa-aquo complexes of nickel(II) and vanadium(III) are analyzed with both ab-initio techniques and UV-VIS-NIR absorption spectroscopy.(2) Second, the excited states of the tetrahedral tetrachloro complex of nickel(II) are investigated, with a special emphasis on the excited states corresponding to formal “two-electron excitations”. In all cases it is shown that the established “electronic energy level” schemes are not sufficient to understand excited-state properties.(3) Mixing of electron configurations varies as molecular structures are modified. Both well-resolved experimental spectra and electronic structure calculations can lead to quantitative insight on such effects.

(1) C. Reber, R. Beaulac, *Comp. Coord. Chem. II* (Elsevier, 2003), Vol. 2, 287-302.

(2) J. Landry-Hum, G. Bussière, C. Daniel, C. Reber, *Inorg. Chem.* 40 (2001) 2595-2601.

(3) F. Baril-Robert, B. Larue, C. Reber, submitted

Oral Presentation

Saturday, 3:00–3:30 PM

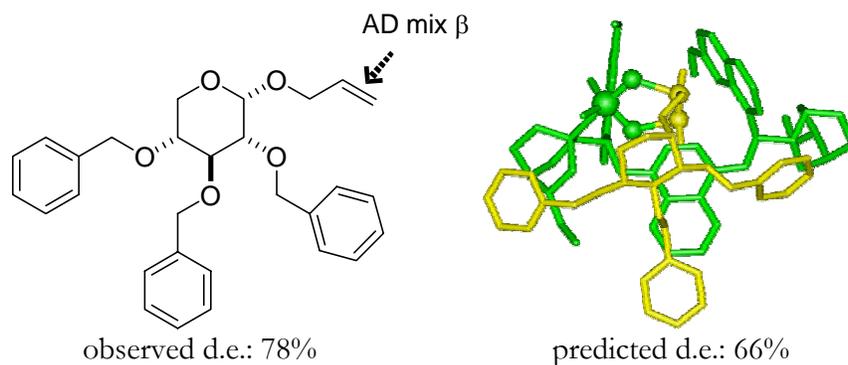
Toward a Computational Tool Predicting the Stereochemical Outcome of Asymmetric Reactions

Nicolas Moitessier

(Dept. of Chemistry, McGill University)

Are the computational methods now ready to be prediction tools of high reliability? A priori assessment of chemistry using computational methods rather than post-facto rationalization of experimental results would indeed have an extraordinary effect on drug, catalysis, and materials discovery.

A dynamic dialog has been initiated in our laboratory between “virtual” and “experimental” chemistry and will be illustrated by a study case. A study on asymmetric dihydroxylation of xylose-based substrates was carried out on both the bench and the screen. We ultimately developed a highly computational predictive tool for this particular reaction.



Oral Presentation

Saturday, 3:30–3:50 PM

Mechanisms of Intramolecular Rearrangements of Cyclic Siloxycarbenes

Paul G. Loncke and Gilles H. Peslherbe

(CERMM and Dept. of Chemistry and Biochemistry, Concordia University)

Hybrid density-functional theory (DFT) calculations, the theory of atoms in molecules (AIM) and the electron localization function (ELF) have been used to investigate the mechanisms of intramolecular rearrangements of 3-sila-2-oxacyclohexylidene. Unique approaches based on these state-of-the-art computational methods have been devised for probing the rearrangement mechanisms. The mechanism for 1,2-H migration has been shown to involve a typical hydride-like shift from the migration origin to the “vacant” carbene. On the other hand, ring contraction has been found to occur via a concerted mechanism involving front-side nucleophilic attack by the carbene lone pair on silicon, as opposed to a stepwise mechanism involving an acyl-silyl biradical intermediate. Lastly, decarbonylation has been shown to be a stepwise reaction that preferentially occurs via the intermediacy of silacyclopentanone rather than acyl-silyl and alkyl-silyl biradicals. Overall, 1,2-H migration and ring contraction turn out to be considerably more favourable than decarbonylation.

Oral Presentation

Saturday, 3:50–4:10 PM

Deducing the Electronic Structure of Nitrilimine

Robert C. Mawhinney, Heidi M. Muchall, and Gilles H. Peslherbe

(CERMM and Dept. of Chemistry and Biochemistry, Concordia University)

The structure of formonitrilimine, HCNNH, has been the subject of various theoretical studies.¹ Based on calculated geometric parameters, it has been assessed that this system is an admixture of mainly two resonance structures, i.e. the propargylic ($\text{HC}\equiv\text{N}-\text{NH}$) and allenic ($\text{HC}=\text{N}=\text{NH}$) forms. Using a combination of density functional theory and wavefunction/electron density analysis tools, such as natural resonance theory (NRT)² and atoms in molecules (AIM)³, we will show that the description of formonitrilimine requires four, nearly equally weighted, resonance structures.

1. K. Kuhler, R. T. Palmer, B. L. Wittkamp and M. R. Hoffmann *J. Mol. Struct. (Theochem)*, 1996, **360**, 41.; M. W. Wong and C. Wentrup *J. Am. Chem. Soc.* 1993, **115**, 7743 and references therein.

2. E. D. Glendening and F. Weinhold, *J. Comput. Chem.*, 1998, **19**, 593.; E. D. Glendening and F. Weinhold, *J. Comput. Chem.*, 1998, **19**, 610.; E. D. Glendening, J. K. Badenhop and F. Weinhold, *J. Comput. Chem.*, 1998, **19**, 628.

3. R. F. W. Bader *Atoms in Molecules*; Oxford University Press: Oxford, 1990.

Oral Presentation

Saturday, 4:10–4:30 PM

Calculation and Assignment of Absorption Spectra of Phenol Radical Cations: 580 nm Absorption of the 3,5-Dimethoxyphenol Radical Cation

L. Zhang, G.H. Peslherbe, H.M. Muchall

(CERMM and Dept. of Chemistry and Biochemistry, Concordia University)

Our preliminary calculations suggest that the Equation-of-Motion Coupled-Cluster Singles and Doubles method (EOM-CCSD), and to a lesser extent the Complete Active Space Self-Consistent Field theory (CASSCF) reproduce the positions of both the primary and secondary bands observed in the UV absorption spectra of methoxy- and methyl-substituted phenols. In this work, these techniques have been applied to calculate the electronic structures and electronic spectra of a variety of methoxy- and methyl-substituted phenol radical cations. The reported abnormally long wavelength in the max 580 nm in λ UV spectrum of the 3,5-dimethoxyphenol radical cation (comparison to the absorption maximum in the spectra of other methoxy-substituted phenol radical cations (between 410 and 460 nm) [1], is qualitatively reproduced by our calculations. In light of the above observation, possible reasons for this finding are explored.

[1] T. A. Gadosy, D. Shukla, L. J. Johnston, J. Phys. Chem. A, 1999, 103, 8834.

Oral Presentation

Saturday, 4:30–4:50 PM

Mechanisms of Flocculation with Poly(ethylene oxide) and Novel Cofactors: Theory and Experiment

Roger Gaudreault, M.A. Whitehead, and T.G.M. van de Ven

(Dept. of Chemistry, McGill University)

In modern papermaking, the use of retention aids, which help to effectively incorporate fines and fillers into a sheet of paper, is widespread. Various single, dual and multi-component retention aid systems are available, one example of which is poly(ethylene oxide) and cofactor, the topic of this thesis. The mechanisms by which such systems function are still poorly understood, thus making the optimization of wet-end papermaking a complex problem. Without a knowledge of the basic mechanisms of these retention aids, costly trial-and-error runs have to be performed. The aim of this thesis is to use Molecular Mechanics (MM) and Semi-empirical Molecular Orbital Theories to test the original ideas and theories, postulating that the association of PEO and cofactor is essential for the flocculation of cellulose fibre fines and that the driving force for association is hydrogen bonding. These theoretical methods provide structures and energies not easily obtainable from experiment, and predict properties and interactions that can be tested experimentally.

Gas phase calculations, using the PM3 Semi-empirical Molecular Orbital Theory, of the interactions between non-ionic poly (ethylene oxide) (PEO), with three model cofactors, (gallic acid, β -1-O-Galloyl-3,6-I-hexahydroxydiphenoyl-D-Glucose (corilagin) and 1,3,6-Tri-O-Galloyl- β -D-Glucose

(TGG)), showed that the delocalised molecular orbitals (DLMO), which describe the bonding between the n-mer (PEO)_n and cofactors, cover the complete complexes. The DLMOs which cover or, traditionally considered as hydrogen bonds, show a distinct “pinch”, a decrease of the electron density between the atoms. Calculations of Gibbs free energy, entropy and enthalpy show that the PEO/cofactor complexes do not form at room temperature, because the loss of entropy exceeds the increase in enthalpy. Even though bond lengths, bond angles, DLMOs and electron densities for the PEO/cofactor complexes are consistent with the definition of hydrogen bonds, the number of inter-molecular and bonds does not correlate with the enthalpy of association of the complexes, indicating that other interactions predominate in the bonding mechanism for this type of system. Moreover this thesis shows that the original idea that the main mechanism of complexation is hydrogen bonding, is incorrect.

Molecular mechanics (MM), molecular dynamics (MD) and PM3 semi-empirical MO theory calculations showed that a complex does not form at room temperature in water, because water weakens the complex.

The mechanisms of flocculation of microcrystalline cellulose (MCC), a model for fibre fines, with poly(ethylene oxide) (PEO) and with various model cofactors: tannic acid (TA), corilagin, polystyrene sulfonated sodium salt (PSS-Na) and folic acid (FA), were studied experimentally using Photometric Dispersion Analysis (PDA). PEO-corilagin interactions were studied by Isothermal Titration Calorimetry (ITC), liquid state proton Nuclear Magnetic Resonance (¹H NMR) and carbon ¹³C NMR. The stability ratios clearly show that TA, corilagin, PSS-Na, FA, PEO, as well as PEO/cofactors, do not flocculate MCC in the absence of salt. ITC shows that PEO (of molar mass 900 kDa) and corilagin do not associate at in the absence of salt, in agreement with the PDA experiments. NMR results show no association between PEO (900 kDa) and corilagin at room temperature in the absence of salt. The ITC and NMR results agree with gas phase PM3 Semi-Empirical Molecular Orbital Theory calculations which show that PEO/corilagin complexes do not form at room temperature in the absence of salt. The association between PEO (of molar mass 10 Mda) and corilagin in the presence of salt (1 mM KCl) has been confirmed by NMR. Consequently, salt is needed to cause MCC flocculation by a PEO-cofactor system. Two types of cofactors have been found: those which cluster PEO in solution (clustering cofactors) and those which do not (non-clustering cofactors). The PEO/TA system flocculates MCC nearly instantaneously by the following mechanism: PEO/cofactor association, followed by PEO-clustering, adsorption and bridging. For the non-clustering cofactors an induction time was observed, which might require process modification for papermaking applications. For the non-clustering cofactors, a new mechanism is proposed to explain the flocculation behaviour of MCC: surface-induced clustering coupled to association-induced polymer bridging.

In summary, the outcome of this work is: (i) three new PEO cofactors were found (corilagin, FA and PSS), (ii) a new flocculation mechanism was formulated: surface-induced clustering coupled to association-induced polymer bridging, and (iii) the PM3 semi-empirical MO theory proved to be predictive of the experimental behaviour of PEO and model cofactors in solution.

Oral Presentation

Saturday, 4:50–5:10 PM

Characterisation of a Novel Self-Association of an Alternating Copolymer into Nanotubes in Solution

Cecile Malardier-Jugroot, T.G.M. van de Ven

*(Dept. of Chemistry and Pulp and Paper Research Centre, McGill University), and
M.A. Whitehead (Dept. of Chemistry, McGill University)*

The characterisation of the association of an alternating copolymer was performed using theoretical methods (quantum mechanics and molecular mechanics) and experimental methods (cryo-Transmission Electron Microscopy, Neutron Reflectivity and Neutron Scattering). The most stable conformation obtained for the self-association at pH 7 using theoretical methods is a tubular structure in which eight SMA molecules make one twist of a helix. The tubes can grow in length by continued regular stacking of benzene rings. The nanotubes have inner and outer diameters of about 28 and 41 Å respectively. The hydrophobic groups are mainly located inside the tube and the hydrophilic groups are mainly on the exterior surface of the tube. They can also associate with themselves creating planes of aligned tubes, which can stack upon each other. The association of alternated copolymer into nanotubes has not been recognized before to the best of our knowledge. The association of SMA octamers into a tubular structure at pH7 was confirmed experimentally by cryo-TEM and the nanotubes observed were several micrometers long. The shape as well as the inner and outer diameter of the nanotubes were also characterised by neutron scattering and the conformation at the air-water interface by neutron reflectivity.

Oral Presentation

Saturday, 5:10–5:40 PM

Theoretical Predictions and Experimental Realizations: Self Assembling Tin-Alkynyl Molecules on Silica Surfaces and Hydrogen Bonded Rosettes of Dinitobenzoic Acid

M.A. Whitehead (Dept. of Chemistry, McGill University),

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Felaniaina Rakotonradany (Dept. of Chemical Engineering, University of Alberta),

Asok Kakkar and Hanadi Sleiman (Dept. of Chemistry, McGill University)

Theoretical background to the experimental realization of molecularly self-assembled thin films will be described, and the ability of theory to predict and design new molecular assemblies surveyed. Then the same ideas will be described in the design and synthesis of photoresponsive and biomimetic supramolecular materials. The need for a thorough integration of theory, with a real understanding of the programmes and their theoretical basis and reliability and experiment where the experimentalist must appreciate the power of theory to predict new structures, and the unreliability of many experiments will be discussed.

Poster Presentation – 1.

Spectroscopy of NaI(H₂O)_n Clusters

*Denise M. Koch, Qadir K. Timerghazin, Gilles H. Peslherbe
(CERMM and Dept. of Chemistry and Biochemistry, Concordia University)
Branka M. Ladanyi (Colorado State University) and James T. Hynes (Ecole Normale
Supérieure, Paris, France, and University of Colorado, Boulder)*

We present a theoretical study of the photodissociation dynamics of NaI(H₂O)_n [n=1-4] clusters. The NaI system has been a prototype system for the study of photodissociation dynamics involving curve crossing of covalent and ionic states. A semiempirical valence-bond approach is employed to describe the electronic structure of NaI, while classical potentials are used for the water-water and ion-water interactions. The cluster photodissociation dynamics, including possible nonadiabatic transitions between the NaI excited and ground electronic states, are simulated with the “molecular dynamics with quantum transitions” method. We show that the excited state population decays faster with increasing cluster size, because of the dynamical stabilization of the outer, ionic branch of the excited state potential by solvent molecules. As demonstrated in previous studies, the reversed polarity of NaI in the Franck-Condon region of the excited state causes the evaporation of 95% to 100% of the water molecules before NaI reaches the curve crossing region, i.e. within 200 fs of excitation. We discuss various probe schemes, photoelectron spectra and infrared spectra in order to monitor the cluster photodissociation in time and make a connection with experiment.

Poster Presentation – 2.

How Many Hydrogen Molecules Can be Inserted into C₆₀?

*Grygoriy A. Dolgonos
(Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland;
CERMM and Dept. of Chemistry and Biochemistry, Concordia University)*

Many possible applications of fullerenes are related to their possibility to form endohedral complexes with atoms (ions) and small molecules. Such complex formation significantly changes the properties of its constituent parts leading even to the formation of such unusual species like He₂ molecule or atomic nitrogen inside the cage. Recently [1], only one H₂ molecule was successfully incorporated inside the C₆₀ cavity after creating an “orifice” in the cage. On the other hand, Erkoç *et al.* [2] claimed that up to 24 hydrogen molecules can form stable endohedral complexes with C₆₀ on the basis of the AM1 calculations (having in mind the application of fullerene for hydrogen storage).

In this study, molecular mechanics with MM+ force field was applied to the endohedral complexes *n*H₂@C₆₀ with *n* = 1–9. The geometry optimization using Polak-Ribiere conjugate gradient algorithm was performed and the interaction (stabilization) energy was calculated as a difference between the energy of the complex and that of its constituent parts. The obtained results revealed that only one hydrogen molecule being incorporated inside the C₆₀ cage form the stable complex in agreement with simple geometrical considerations and the experimental data [1]. The reliability of semiempirical methods to study the problem of H₂ insertion into C₆₀ is discussed.

1. Y. Murata, M. Murata and K. Komatsu, *J. Am. Chem. Soc.*, **2003**, *125*, 7152.
 2. L. Türker and S. Erkoç, *J. Mol. Struct. (Theochem)*, **2003**, *638*, 37.
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Poster Presentation – 3.

Computational Studies of N-phenyl-N'-sulfinylhydrazines: Factors Influencing Dimerization

Pratibha Malla and Heidi M. Muchall

(CERMM and Dept. of Chemistry and Biochemistry, Concordia University)

Geometries, energies and frequencies of N-phenyl-N'-sulfinylhydrazine (Ph-NH-N-S=O) and its chloro and methyl derivatives (ortho, meta and para substituted) have been studied in the gas phase and in solution at the B3LYP/6-31+G(d) level of theory. Solution studies have been done in carbontetrachloride ($\epsilon = 2.22$), chloroform ($\epsilon = 4.9$), dichloromethane ($\epsilon = 8.93$) and methanol ($\epsilon = 32.63$) using the self-consistent reaction field (SCRf) theory with the conductor-like screening model (COSMO). The computed data are compared with available experimental data. The magnitude of the red shift in the N-H stretching vibrational frequencies upon dimerization is found to be in good agreement with experiment. Wave functions have been analyzed with the theory of atoms in molecules to identify atomic interactions to explain observed geometries. In order to understand the observed trends in the stability of the Ph-NH-N-S=O dimers, N-H and S=O bonds for a variety of aromatic substituents (F, Cl, Br, Me, Ome, CN, NO₂, OH) have been analyzed in terms of electron densities. Several Hammett-type correlations will be discussed.

Poster Presentation – 4.

Computational Study of Complex Formation and Reaction of N-Sulfinylamines with Water

Elena Ivanova and Heidi Muchall

(CERMM and Dept. of Chemistry and Biochemistry, Concordia University)

The reaction of N-sulfinylamines with water was one of the first properties of this new class of compounds observed in the 1890s, and their stability towards hydrolysis depends on their structure.¹ Later it was shown experimentally that the formation of pre-reaction complex of the N=S=O species with water or alcohol represents the rate determining step in these reactions, which are catalyzed by bases.^{2,3} Also the formation of a weakly bonded complex of the sulfur atom of N-sulfinyl compounds with the nitrogen atom of aromatic and aliphatic amines in solution was proposed.⁴ The study of the complexation and reaction of the N=S=O group in N-sulfinylamines with some model compounds (including water, methanol and amines) was performed at different levels of theory, considering the counterpoise correction and simulation of the solvent field by the conductor-like screening model (COSMO). The B3LYP method with the 6-31+G(d) basis set was confirmed to be the overall best choice, combining satisfactory conformity of calculated and experimental result and relative computational economy for the large systems. The nature and the strength of the interactions are discussed within the framework of the "Atoms in molecules" (AIM) and "Natural bond orbital" (NBO) theories and compared to other similar donor-acceptor complexes.

(1) Michaelis, A. Chem. Ber. 1889, 22, 2228-2233.

(2) Mironova, D. F.; Konoplya, O. Y. Ukr. Khim. Zn. 1976, 42, 374-378.

(3) Mironova, D. F.; Konoplya, O. Y. Ukr. Khim. Zn. 1976, 42, 960-961.

(4) Cerioni, G.; Culeddu, N.; Plumitallo, A. Tetrahedron 1993, 49, 2957-2964.

Poster Presentation – 5.

Computational Studies of Intramolecular Agostic Ancillary Ligand–Metal Interactions in Cationic Zirconocenium Complexes.

*Svetlana Popenova, Philippe G. Merle and Gilles H. Peslherbe
(CERMM and Dept. of Chemistry and Biochemistry, Concordia University)*

Many chemical processes involve agostic-type interactions between ligands and transition metal cations. For example, agostic interactions in zirconocenium cationic complexes, which are believed to be active catalytic species for α -olefin polymerization, play a key role in reactivity of the catalyst and resulting polymeric structure. In this work, we are interested in possible agostic intramolecular interactions between bulky substituents on the cyclopentadienyl rings and a metal center in the zirconocenium cationic species with general formula: $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4\text{R}\}_2\text{Me}]^+$ or $[\text{Zr}\{3,3'\text{-Si}(\text{Me})_2(\eta^5\text{-C}_5\text{H}_3\text{R})_2\}\text{Me}]^+$, where $\text{R} = \text{H}$, SiMe_2Y ; $\text{Y} = \text{-Me}$, -F , $\text{-(CH}_2)_n\text{CF}_3$, and how these interactions, would influence the coordination of the ethylene to the metal center of the complexes. A combination of Density Functional Theory (DFT) and the quantum theory of Atoms In Molecule (AIM), was used to investigate this issue. We will report structures, energies and electronic properties of different complexes, focusing on possible intramolecular agostic-type interactions. Future directions will also be discussed.

Poster Presentation – 6.

Theoretical Study of Tunnelling in Proton Transfer Laser Dyes: The 2-(2'-Hydroxyphenyl)Benzimidazole as a Test Case

*Sacha Zlatkova (CERMM and Dept. of Chemistry and Biochemistry, Concordia University)
Zorka Smedarchina (Steacie Institute for Molecular Sciences, NRC)*

Due to its very high fluorescence quantum yield, 2-(2'-hydroxy-phenyl) benzimidazole (HBI) is a representative of a class of laser dyes based on proton transfer which are of practical interest as efficient energy sources. The dynamics of proton transfer in the ground and first excited singlet state are studied in order to elucidate the role of tunneling in the very fast (within picoseconds) tautomerization taking place after photo-excitation. As input parameters we use the results of standard electronic structure and force field calculations carried out by the AM1 semi-empirical method at the three stationary points of the potential energy surfaces of the ground and first singlet excited states. For each electronic state, the transfer is treated as a one-dimensional process along an effective proton coordinate. The rate constant is expressed as a sum of a classical and tunnelling components, and the latter is evaluated with a generalized quasi-classical approach, which yields the correct zero-temperature limit. It is demonstrated that, for the set of AM1 parameters, proton transfer in the photochemical cycle of HBI is dominated by tunneling even at room temperature, the classical mechanism being less probable by orders of magnitude.

Poster Presentation – 7.

Computational Studies of the Reactivity of Vanadium Oxide Clusters towards Halocarbons

Yin Wei and Gilles H. Peslherbe

(CERMM and Dept. of Chemistry and Biochemistry, Concordia University)

Vanadium oxide compounds are important industrial catalysts for the oxidation and functionalization of various chemical compounds.¹ Studies of gas-phase vanadium oxide clusters provide an avenue to explore the reactive sites implicated in surface catalysis.² Castleman and co-workers³ have reported an extensive amount of experimental data on the gas-phase reactions of vanadium oxide clusters with environmentally relevant halocarbons. Computational studies will help further our understanding of the elementary step of the reaction of vanadium oxide clusters towards halocarbons. Density-Functional Theory (DFT) calculations are employed to study the reactivity of vanadium oxide clusters. The proposed oxygen transfer pathway in the reaction between $V_2O_4^+$ and CH_2F_2 is confirmed by our calculations. Our results suggest that charge densities, ionization potentials, binding energies and oxidation states of vanadium oxide clusters influence the reactivity of vanadium oxide clusters towards halocarbons. This may help explain why a higher reactivity is observed experimentally for the smaller vanadium oxide clusters with CH_2F_2 while the reactivity of vanadium oxide clusters with CH_3CF_3 is rather insensitive to cluster size.

1. Weckhuysen, B. M.; Keller, D.E. *Catal. Today* **2003**, *78*, 25-46

2. Zemski, K.A.; Justes, D. R.; Castleman, A. W. *J. Phys. Chem. B* **2002**, *106*, 6136-6148

3. Bell, R.C.; Zemski, K.A.; Castleman, A. W. *J. Phys. Chem. A* **1998**, *102*, 8293-8299; *J. Phys. Chem. A* **1999**, *103*, 2992-2998; *J. Phys. Chem. A* **1999**, *103*, 1585-1591

Poster Presentation – 8.

Implementation of Functionality QM/MM in DeFT and Application to Calculations of the Free Energy

*Etienne Paradis (CERMM and Dept. of Chemistry and Biochemistry, Concordia University)
and Alain St-Amant (Dept. of Chemistry, University of Ottawa)*

We implemented functionality QM/MM by interfacing the Roar with density functional software package (DeFT). This QM/MM approach allows one to model very large molecular systems: the few atoms essential to a system's reactivity are treated by QM means while all other atoms are handled at the simple MM level. We use this new functionality to optimize a method for free energy calculation by combining AM1/DeFT. Results of reaction in gas phase and solution will be presented.

Poster Presentation – 9.

A Preconditioned Iterative Method for Studying the Acetylene/Vinylidene Isomerization

*Jean Christophe Tremblay and Tucker Carrington Jr.
(Département de chimie, Université de Montréal)*

The isomerization of acetylene to vinylidene is studied theoretically using a global potential energy surface. The exact Hamiltonian for zero total angular momentum is written in C_2-H_2 diatom-diatom Jacobi coordinates in order to exploit the full symmetry of the system. Its eigenvalues/eigenfunctions are calculated using a new approach based on an efficient combination of contracted basis functions with iterative methods. The Preconditioned Inexact Spectral Transform (PIST) Lanczos method is used to extract at a minimal cost the eigenvalues and eigenvectors of the full 6D problem in a selected energy window near the expected vinylidene ground state. The use of block-Jacobi rotations to minimize the off-diagonal elements of the Hamiltonian matrix and of a so-called Wyatt block renders the preconditioner, and thus the algorithm, very efficient. States with clear vinylidene-like characteristics can be identified by graphical analysis of the associated eigenfunctions.

Poster Presentation – 10.

Quantum Monte Carlo Simulations of $I^-(H_2O)_n$ and $Na^+(H_2O)_n$ Clusters (n=12, 20)

*Mouna Sbata and Gilles Peslherbe
(CERMM and Dept. of Chemistry and Biochemistry, Concordia University)*

Quantum effects are expected to be significant in low-temperature ionic aqueous clusters, as hydrogen atoms are light and hydrogen bonds are weak. Quantum effects may affect the cluster structural properties and thermodynamic properties such as binding enthalpies, and these effects may become increasingly important at low temperatures (below 100K). In this work, we present structural properties (radial probability distributions) and binding enthalpies of $I^-(H_2O)_n$ and $Na^+(H_2O)_n$ (n=12, 20) clusters at 70 K and 300 K from Quantum Path Integral Monte Carlo simulations with pairwise additive potentials. A comparison is done between our results and previous simulations which were carried out classically. The influence of quantum effects on the cluster structural properties and thermodynamics is discussed.

Poster Presentation – 11.

Electronic Structure and Radiative Lifetimes of the LaF⁺ Radical

Mouna Sbata and Joël Schamps

(Université des Sciences et Technologies de Lille, Villeneuve d'Ascq, France)

SCF-MRCI calculations have been performed to determine the electronic structure of the LaF⁺ radical (<52000 cm⁻¹). This ab initio study allows us to confirm that the ground state of the radical is X²Δ as suggested by L.A. Kaledin et al.(1) and its first excited state is the doublet ²Σ⁺. This is surprising when we know that for the isoelectronic system of LaF⁺, the neutral molecule LaO, the reverse order is observed. We will see how this is possible. A radiative dynamic study permits to calculate the Einstein coefficients, oscillator strengths and radiative lifetimes of the first excited electronic states of the radical.

1. L.A. Kaledin, A.L. Kaledin, M.C. Heaven, J. Mol. Spectrosc., 179, 246 (1996)

Poster Presentation – 12.

Spin-Dependent Transmission Through Periodically Stubbed Waveguides Due to Spin-Orbit Interaction: Influence of Subband Mixing

X. F. Wang, P. Vasilopoulos (Dept. of Physics, Concordia University), and F. Peeters (Universiteit Antwerpen, Antwerpen, Belgium)

Ballistic spin transport, through periodically stubbed waveguides, is studied in the presence of a weak spin-orbit interaction (SOI) and the resulting subband mixing. By an appropriate choice of the waveguide length and of the stub parameters injected spin-polarized electrons can be blocked completely and the transmission shows a periodic and nearly square-wave pattern with wide gaps when only one mode is allowed to propagate in the waveguide. Relative to the case when subband mixing is neglected, the transmission changes drastically as a function of the incident electron energy or of the stub height, as it exhibits new peaks or dips, but remains robust as a function of the stubs' degree of asymmetry. Varying the strength of the SOI parameter changes the relative contribution to the total transmission of the spin-up and spin-down states. The structure considered is a good candidate for establishing a realistic spin transistor.

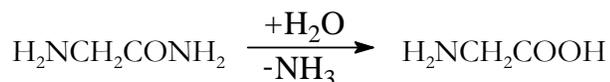
Theoretical Study of the Mechanism of Aminoacetonitrile Hydrolysis

Sichuan Xu, Gilles H. Peslherbe

*(CERMM and Dept. of Chemistry and Biochemistry, Concordia University) and
James T. Hynes (Ecole Normale Supérieure, Paris, France; University of Colorado at Boulder)*

Amino acids formed in the interstellar medium (ISM) and delivered to the Earth could have played a pivotal role in the prebiotic chemistry of the early Earth, since they are basic components of proteins that are essential constituents of all organisms. One of the possible routes to generate amino acids is through the Strecker synthesis. Our previous work has indicated that a precursor of glycine [$\text{H}_2\text{NCH}_2\text{COOH}$], aminoacetonitrile [$\text{H}_2\text{NCH}_2\text{CN}$], is effectively generated from the simpler molecules of CH_2NH , HNC (or HCN) and H_2O in the cold ISM. In this work the mechanism of aminoacetonitrile hydrolysis to produce glycine and ammonia will be presented.

Gas-phase quantum chemistry calculations with the B3LYP/6-311+G(d,p) model chemistry suggest that the hydrolysis mechanism involves 4 steps:



All stationary points have been optimized and characterized by frequency calculations, and reaction paths have been determined by calculations of Intrinsic Reaction coordinate (IRC). Our results demonstrate that the mechanism of aminoacetonitrile hydrolysis is complex, and in the gas phase the hydrolysis is unlikely, due to the high reaction barriers of key steps (~ 50 kcal/mol). The role of additional water molecules in the hydrolysis of aminoacetonitrile is being investigated.

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