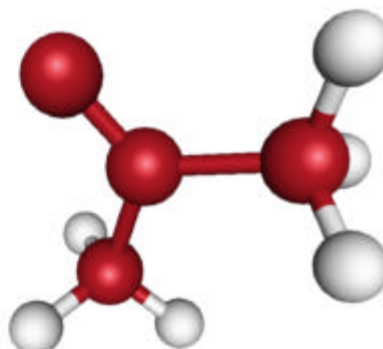




Concordia
UNIVERSITY



CERMM

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

Third Annual CERMM Symposium

January 10-11, 2003

De Sève Theatre, McConnell Building
Concordia University
1400 De Maisonneuve Blvd, Montréal

The mission of the Centre for Research in Molecular Modeling (CERMM) is to foster collaborations between researchers in computational chemistry and biochemistry within and between institutions, to provide an interdisciplinary forum for experimentalists and theoreticians to combine their expertise to model and understand natural phenomena at the molecular level, and to promote excellence in graduate training in the computational sciences.

The Annual Symposium of the Centre for Research in Molecular Modeling is meant to provide a unique opportunity for graduate students and researchers to share their interest in computational chemistry and biochemistry research in an informal setting. On behalf of all CERMM members, let me take the opportunity to welcome you all to our Third Symposium and we anticipate that it will be an enjoyable event.



Gilles Peslherbe,
CERMM Director

For more information on CERMM, please consult
<http://artsci-cwin.concordia.ca/chem/CERMM>

SYMPOSIUM PROGRAM

FRIDAY, JANUARY 10, 2003

- 2:15** Opening Remarks
Marcus Lawrence, Chair, Dept. of Chemistry and Biochemistry
Gilles H. Peslherbe, Director, Centre for Research in Molecular Modeling
- 2:30** Plenary Lecture
Tom Ziegler, University of Calgary
Density Functional Theory as A Practical Tool in Transition Metal Chemistry
- 3:30** Coffee
- 4:00** **Alain Rochefort**, Ecole Polytechnique
Low dimensional Organic Materials for Nanoelectronics
- 4:40** **Robert C. Mawhinney** and Georg Schreckenbach, Concordia University
NMR Quantum Computing: Applying Theoretical Methods to Designing Enhanced Molecular Systems
- 5:00** **Elisa Fadda**, Mark Casida and Dennis Salahub, Université de Montréal
Assessment of the Strengths and Limitations of SOS-DFPT Throughout the Entire Range of the (14,15)N NMR Shielding Spectrum
- 5:20** **Armand Soldera**, Université Sherbrooke
The Glass Transition of PMMAs Studied by Molecular Modeling
- 6:00** Symposium Dinner (\$20)

SATURDAY, JANUARY 11, 2003

- 9:00** Coffee
- 9:30** **Francois G. Amar** and Jinasena Hewage, University of Maine
Structure and Thermodynamics of $Ar_m(N_2)_n$ Clusters
- 10:10** **Sean R. Hughes**, Tao-Nhan Nguyen, John A. Capobianco and Gilles. H. Peslherbe, Concordia University
Modeling the Structure and Thermodynamics of Ln^{3+} -Water Clusters ($Ln=Nd, Eu, Er, Yb$)

10:30 Coffee

11:00 Denise Koch, Qadir Timerghazin, Gilles Peslherbe, Branka M. Ladanyi and James T. Hynes, Concordia University
Nonadiabatic Trajectory Studies of Photodissociation Dynamics in NaI(H₂O)_n Clusters

11:20 Andrew Ryzhkov, and Parisa Ariya, McGill University
A Theoretical Investigation of the Reactions of Parent and Substituted Carbonyl Oxides with Water Under Near Atmospheric Conditions

12:00 Lunch – Poster Session

2:00 Xiaogang Wang, and Tucker Carrington Jr, Université de Montréal
Vibrations of Methane: an Exact Numerical Solution of a Nine-Dimensional Schrödinger Equation

2:40 Qadir Timerghazin, and Gilles Peslherbe, Concordia University
The Acetonitrile Dimer Anion: Structure, Stability, and Atoms-In-Molecules (AIM) Analysis

3:00 Heidi Muchall, Petrina Kamy and Jean Lessard, Concordia University and Université de Sherbrooke
The Conformational Behavior of Methylenecyclohexanes Revisited

3:20 Adam Dickie, Ashok Kakkar and **Tony Whitehead**, McGill University
Self-Assembled Alkynyl Thin Films: Theoretical Evaluation and Experimental Fabrication

4:00 Coffee

4:30 Céline Toubin, David Yeung, **Ann English** and Gilles Peslherbe, Concordia University
Theoretical Evidence for the Catalytic Role of Copper Metal Ions in the Degradation of S-Nitrosothiols

4:50 Régis Pomès, University of Toronto
Molecular Determinants of Biological Proton Transport

5:30 Closing – Poster Session

POSTERS

- P1** **P. Guay** and A. Rochefort, INRS Énergie, Matériaux et Télécommunications and École Polytechnique de Montréal
Improved Hydrogen Adsorption Capacity of Doped-Carbon Nanotube Bundles
- P2** **E.V. Ivanova** and Heidi M. Muchall, Concordia University
Computational Studies of Hydrolysis of N-sulfinyl-compounds
- P3** A. Rochefort, **M. Layachi**, R. Martel, Ph. Avouris and Y. Savaria, École Polytechnique de Montréal and Centre de recherche en calcul appliqué
Electron Transport into Organized Low-Dimensional Molecular Systems
- P4** **E. Paradis** and A. St-Amant, University of Ottawa
Introducing the QM/MM Functionality within the DeFT Software Package and Its Application to Free Energy Calculations
- P5** **S. Popenova**, R. C. Mawhinney and G. Schreckenbach, Concordia University
Theoretical Studies of Lithium Hexamethyl Disilazide Complexes: Effects of Solvation and Aggregation
- P6** F. Rakotondradany, **M. A. Whitehead** and H. F. Sleiman, McGill University
Photoresponsive Supramolecular Systems: Self-Assembly of Azodibenzoic acid Linear Tapes and Cyclic Tetramers
- P7** T. Carrington Jr. and **J. C. Tremblay**, Université de Montréal
Calculation of resonance energies and widths of HCO using a novel Lanczos-based method
- P8** **D. Yong-Hoi Yeung**, G. H. Peslherbe and A. M. English, Concordia University
Structural elucidation of calbindin D_{28K} with intramolecular cross-linkers, mass spectrometry and molecular mechanics
- P9** M. Zhuang and **M. Ernzerhof**, Université de Montréal
Structure and Spin Relaxation of Rh_n ($n=2-15$) Cluster
- P10** **T.-N. V. Nguyen**, G. H. Peslherbe and H. Vach, Concordia University and Ecole Polytechnique (France)
Molecular vibrational excitation in surface-induced fragmentation of $(O_2)_m$ and $(N_2)_m$ clusters
- P11** M. Sbata and **G. H. Peslherbe**, Concordia University
Quantum and Classical Monte Carlo Simulations of $\Gamma(H_2O)_n$ clusters ($n=12, 20$)

- P12** **P. R.N. Kamy** , H. M. Muchall and J. Lessard, Concordia University and Université de Sherbrooke
Conformational Studies of Substituted Cyclohexanes
- P13** **M.R. Harpham**, N.E.Levinger, B.M. Ladanyi and K.W. Herwig, Colorado State University and ORNL
Water Mobility in Small Aerosol OT Reverse Micelles
- P14** **Y. Wei**, P. Larrégaray and G. H. Peslherbe, Concordia University
Theoretical Studies of the Photo-Induced Dissociation of Metal Clusters
- P15** **P. G. Loncke** and G. H. Peslherbe, Concordia University
A Theoretical Study of the Ring Contraction of 3-Sila-2-oxacyclohexylidene and 2-Oxacyclohexylidene
- P16** C. Malardier-Jugroot, T.van de Ven and **M.A.Whitehead**, McGill University
Neutron Reflectivity Study of poly(styrene Maleic Anhydride) at the Air Water Interface: Theory and Experiment
- P17** F. Rakotondradany, H.Sleiman and **M.A.Whitehead**, McGill University
Photoresponsive supramolecular systems:Self-assembly of azodibenzoic acid linear tapes and cyclic tetramers; theory and experiment
- P18** **J. Smaby** and F. G. Amar, University of Maine
Stationary States of Model Systems by Damped Bohm Dynamics
- P19** **J. Smaby** and F. G. Amar, University of Maine
Polarization Energies of Mixed Xe/Ar Cluster Ions
- P20** **C. Romanescu**, S. Manzhos, D. Boldovsky and H.-P. Looock, Queen's University
Photodissociation Dynamics of HCl. Experimental Data and Modelling of the Superexcited States
- P21** **P. Ayotte**, Université de Sherbrooke
Ionic Dissociation of Molecules in Clusters and on Ice Surfaces
- P22** **R. Gaudreault**, T.van de Ven and M.A.Whitehead, McGill University
Molecular Modelling of Poly(ethylene Oxide), Model Cofactors, and their Interactions with Water
- P23** V. Tessier, M. Ernzerhof and D. Zargarian, Université de Montréal
Density Functional Theory Study of Nickel Indenyl Complexes as Catalysts

ABSTRACTS

Plenary Lecture – Friday, 2:30 pm

Density Functional Theory as A Practical Tool in Transition Metal Chemistry

Tom Ziegler

University of Calgary, Calgary

Approximate density functional theory (DFT) [1] has over the past decade emerged as a tangible and versatile computational method in organic as well as inorganic chemistry. DFT affords molecular structures [2], vibrational frequencies [3], bond dissociation energies [4] as well as NMR [5a] and ESR parameters [5b] comparable in accuracy to high level ab initio methods, at a fraction of their cost. The method is further able to trace energy profiles for elementary reaction [6] steps and provide accurate estimates [7] of activation energies. DFT can also be used to simulate reaction dynamics [8] and incorporate solvent effects as well as the steric bulk of large ligands through a combined DFT and Molecular Mechanics approach [9]. A discussion will be given of how DFT can be used to solve problems in transition metal chemistry and catalysis [10].

1. (a) T. Ziegler, *Chem. Rev.* 91, 651 (1991). (b) T. Ziegler, *Can. J. Chem.* 73, 743 (1995).
2. L. Fan and T. Ziegler, *J. Chem. Phys.* 95, 7401 (1991).
3. (a) L. Fan and T. Ziegler, *J. Chem. Phys.* 96, 9005 (1992). (b) L. Fan and T. Ziegler, *J. Phys. Chem.* 96, 6937 (1992). (c) A. Berces and T. Ziegler, *Top. Cur. Chem.* 182, 42 (1996).
4. E. Folga and T. Ziegler, *J. Am. Chem. Soc.* 115, 5169 (1993).
5. (a) G. Schreckenbach and T. Ziegler, *J. Phys. Chem.* 99, 606 (1995). (b) G. Schreckenbach and T. Ziegler, *J. Phys. Chem. A* 101, 3388 (1997).
6. L. Deng and T. Ziegler, *Int. J. Quant. Chem.* 52, 731 (1994).
7. L. Fan and T. Ziegler, *J. Am. Chem. Soc.* 114, 10890 (1992).
8. P. Margl, J.C.W. Lohrenz, T. Ziegler and P. Blöchl, *J. Am. Chem. Soc.* 118, 4434 (1996).
9. T.K. Woo, P.M. Margl, P.M. Blöchl and T. Ziegler, *J. Phys. Chem. B* 101, 7877 (1997).
10. L. Deng, T.K. Woo, L. Cavallo, P.M. Margl and T. Ziegler, *J. Am. Chem. Soc.* 119, 6177 (1997).

Low dimensional Organic Materials for NanoelectronicsAlain Rochefort*École Polytechnique de Montréal, Engineering Physics Department and Centre de recherche en calcul appliqué (CERCA), Groupe Nanostructures, Montréal*

The possibility of using new forms of organic-based materials for practical applications in nanoelectronics has stimulated an important amount of exciting works during the last decade. For example, since their discovery in 1991, carbon nanotubes (CNTs) have been used as an active component in the fabrication of transistor, memory elements, and more recently, logic circuits. CNT's can also be used as a template for nanofabrication and as reservoirs for the storage of gas, ions, or metals. In this respect, it has been recently shown experimentally that multiple C₆₀ molecules can penetrate into a carbon nanotube to form a one-dimensional array of C₆₀ nested inside. This new type of carbon materials, due to its original structure, is often called carbon peapod. Although recent STM results show drastic modification of the local electronic structure of semiconducting nanotube peapods, I will show that the electronic as well as the electron transport properties of exothermic peapods do not show drastic differences from the properties of individual species. However, the CNT-C₆₀ interaction increases slightly as the nanotube diameter decreases, but becomes very important for endothermic peapods.

NMR Quantum Computing : Applying Theoretical Methods to Designing Enhanced Molecular Systems.Robert C. Mawhinney and Georg Schreckenbach*Department of Chemistry and Biochemistry and Centre for Research in Molecular Modeling, Concordia University, Montréal*

“Molecular Memory Bank Draws Closer” reads one of the BBC online news headlines of December 3, 2002. This is perhaps the first *general public* report on NMR quantum computing. The proposal for using NMR techniques for quantum computing was introduced only 6 years ago. Despite the gains made so far, many believe that the potential for NMR quantum computing is very limited, and building systems with more than 10 qubits is practically impossible (a qubit is a quantum bit, in this case it is typically an atom with a nuclear spin of 1/2). So, this first “real life” implementation, using 19 qubits, not only exceeds this limit but demonstrates a practical application of the methodology. The two main challenges to implementing NMR quantum computing are: (1) the control of pulse imperfections and (2) the design of molecules with enhanced spectral properties, in particular chemical shifts and spin-spin coupling constants. The predictive nature of theoretical chemistry is particularly geared towards exploring the latter challenge. We will present calculated chemical shielding and spin-spin coupling constant results for a number of systems already used for testing NMR quantum computing algorithms. From these results we will assess some of the design criteria required for molecules to be used in NMR quantum computing. From these criteria new, enhanced, systems may be proposed. Future work based on these findings will be discussed.

Assessment of the Strengths and Limitations of SOS-DFPT Throughout the Entire Range of the (14,15)N NMR Shielding Spectrum

Elisa Fadda,^(1,2) Mark E. Casida⁽³⁾ and Dennis R. Salahub^(1,2,4)

(1) *Université de Montréal, Département de Chimie, Montréal*, (2) *Centre de Recherche en Calcul Appliqué (CERCA), Montréal*, (3) *Laboratoire des Etudes Dynamiques et Structurales de la Sélectivité (LEDSS) Université Joseph Fourier, Grenoble, France*, (4) *University of Calgary, Calgary, Alberta*

The ab-initio determination of the Nuclear Magnetic Resonance (NMR) shielding tensor has in recent years attained a sufficient level of accuracy to be used as a support tool for experimental research. The usefulness of this tool in practical applications is governed both by its reliability and by its computational cost. Density-Functional Theory (DFT) has come to play a leading role in the calculation of chemical shift tensors. In this work we evaluate the strengths and limitations of Sum-Over-States Density-Functional-Perturbation Theory (SOS-DFPT) in the NMR shielding's calculation of nitrogen, a nucleus widely recognized as a challenging case for chemical shift calculations. The 14,15N NMR shielding has been determined for 131 different nitrogen atoms types and the results are compared to experimental shieldings, determined in aprotic solvents. Since the calculations cover virtually the whole range of nitrogen NMR chemical shift spectra, in order to obtain significant conclusions, the results have been analysed and discussed within groups of similar molecular systems. The understanding of the maximum errors and of the capabilities of the various approximations used in SOS-DFPT for each type of nitrogen atom allows its use as a support tool for the interpretation of experimental NMR spectra.

The Glass Transition of PMMAs Studied by Molecular Modeling

Armand Soldera

Département de Chimie, Université de Sherbrooke, Sherbrooke

From an experimental viewpoint, dilatometric technique is currently employed to determine the glass temperature transition, T_g : the specific volume is reported versus the cooling temperature. It was shown that molecular simulation could achieve this physical property using molecular dynamics. As a matter of fact, energetic analysis and microscopic investigations can be carried out to understand the glass transition phenomenon. Among polymers, PMMA, poly(methyl methacrylate), provides a real center of interest since the difference in T_g s between the two configuration chains can be interpreted only in changes in molecular characteristics. As a matter of fact, simulated dilatometry techniques have been applied to compute the T_g s of the two PMMA chain tacticities, and PMA, poly(methyl acrylate). An energetic analysis showed that the non-bond energy and the bending angle energy associated to the intradiad backbone angle, principally contribute to the energetic difference between the two PMMA configurations. These two energetic contributions resulted from the substitution of the hydrogen atom attached to the chiral carbon atom in the PMA repeat unit by a methyl group. Such a substitution also implies a variation in the local dynamics. In order to reveal local motions, correlation times were computed. They are firstly compared to experimental data acquired from NMR spectroscopy. From this validation step, flexibilities of the backbone and the side-chain can be looked at. They were found to be different according to the chain configuration. Following the free volume theory, the two energetic variations and the difference in the local motions allowed for an increase in T_g in comparison to PMA, and to an enlargement of the difference in the T_g s between the two PMMA configurations. The same behavior was encountered with the two PEMA, poly(ethyl methacrylate), chain tacticities.

Structure and Thermodynamics of $\text{Ar}_m(\text{N}_2)_n$ Clusters

François G. Amar and Jinasena W. Hewage

Department of Chemistry, University of Maine, MA

Using realistic pair potentials, we investigate the structures of mixed clusters of argon and nitrogen in order to interpret the experimental electron diffraction patterns reported by the Torchet group. Simulations of small clusters indicate that argon tends to segregate at the center of the clusters. We report on the structure and thermodynamics of the 13-mers of varying stoichiometry. For larger clusters, in the range of 50 to 200 molecules, we predict electron diffraction patterns with those recorded in the experiments. The models allow us to estimate the average size and composition of the mixed clusters for a given set of experimental conditions (nozzle pressure and Ar partial pressure).

Modeling the Structure and Thermodynamics of Ln^{3+} -Water Clusters ($\text{Ln}^{3+}=\text{Nd}^{3+}, \text{Eu}^{3+}, \text{Er}^{3+}, \text{Yb}^{3+}$)

Sean R. Hughes, Tai-Nhan Nguyen, John A. Capobianco and Gilles H. Peslherbe

Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University, Montréal

The properties of hydrated, metal-ion clusters or $[\text{M}(\text{H}_2\text{O})_n]^{m+}$ has been the focus of much research over the years. In an effort to predict the behavior of clusters containing solvated Ln^{3+} metal ions, we have chosen to develop model potentials based on high-level, quantum, QCISD(T) calculations of small Ln^{3+} -water dimers ($\text{Nd}^{3+}, \text{Eu}^{3+}, \text{Er}^{3+}, \text{Yb}^{3+}$). The model contains expressions to describe Coulombic, polarization and repulsion-dispersion interactions. The coordination number of the Ln^{3+} ion within the first hydration shell is cluster size dependent. Energetic properties of the clusters, for instance the internal energy of the cluster, are reproduced well with respect to clusters of an equivalent size calculated at the ab-initio level. Finally, the convergence of structural and thermodynamic properties towards bulk-like values is only achieved at very high cluster sizes ($N > 64$). This reflects the extensive range of influence that the lanthanide ions have on their surroundings.

Nonadiabatic Trajectory Studies of Photodissociation Dynamics in NaI(H₂O)_n ClustersDenise M. Koch,⁽¹⁾ Qadir K. Timerghazin,⁽¹⁾ Gilles H. Peslherbe⁽¹⁾Branka M. Ladanyi⁽²⁾ and James T. Hynes⁽³⁾

(1) Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry Concordia University, Montréal, (2) Department of Chemistry, Colorado State University, Fort Collins, (3) Département de Chimie, CNRS, Ecole Normale Supérieure, Paris, and Department of Chemistry & Biochemistry, 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 water-ion 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 possible probe schemes in order to monitor the cluster photodissociation in time and make a connection with experiment.

A Theoretical Investigation of the Reactions of Parent and Substituted Carbonyl Oxides with Water under Near Atmospheric Conditions

Andrew Ryzhkov and Parisa Ariya

McGill University, Department of Atmospheric and Oceanic Sciences, Montréal

Carbonyl oxide is a well-known intermediate formed in gas-phase reactions of ozone with alkenes. Secondary reactions of carbonyl oxide are suggested to lead to the formation of HO_x, H₂O₂ and organic peroxides in the atmosphere. We performed a theoretical study of reactions of carbonyl oxides series with water and a water dimer. Using CCSD(T)/6-311+G(2d,2p)//B3LYP/6-311+G(2d,2p) calculations we found that the most energetically favourable channels are the formation of alpha-hydroxy hydroperoxide as the result of reactions of carbonyl oxide with the water and water dimer. The potential importance of water dimer reactions in the chemistry of the troposphere is discussed herein.

Saturday, 2:00 – 2:40 pm

Vibrations of Methane: an Exact Numerical Solution of a Nine-Dimensional Schrödinger Equation

Xiao-Gang Wang and Tucker Carrington Jr.

Département de Chimie, Université de Montréal, Montréal

The quantum description of molecular vibrational states is a subject of great interest. We solve the Schrödinger equation numerically using the variational method. Variational calculations are very expensive. It has been a decade since the first variational calculation of the vibrational levels of four-atom molecules (in six dimensions). Only very recently the first calculations for a five-atom molecule (methane) have appeared in the literature. In this talk, I summarize our recent work on the variational calculation of vibrational levels of methane in nine dimensions. We use a method that employs simply contracted basis functions in conjunction with the Lanczos algorithm to calculate a spectrum. The basis functions represent the desired wavefunctions well, yet are simple enough that matrix-vector products may be evaluated efficiently. A large number of vibrational levels on a good global *ab initio* potential surface are well converged. These include almost all the states up to 8000 cm^{-1} and some higher local mode stretch bands. The calculated levels agree well with experimental data.

Saturday, 2:40 – 3:00 pm

The Acetonitrile Dimer Anion: Structure, Stability, and Atoms-In-Molecules (AIM) Analysis

Qadir K. Timerghazin and Gilles H. Peslherbe

Centre for Research in Molecular Modeling and Department of Chemistry and Biochemistry, Concordia University, Montréal

The acetonitrile dimer anion $(\text{CH}_3\text{CN})_2^-$ was recently observed in the experimental studies of the relaxation of photoexcited iodide-acetonitrile clusters, but its structure and stability are still unknown. In this work, *ab initio* calculations of possible acetonitrile dimer anion isomers, their stability, and electron binding energies will be presented. Topological analysis of electron density distribution in the framework of Atoms-In-Molecules theory will be applied to get further insight into the electronic structure of the "dipole-bound" and "solvated electron" forms of $(\text{CH}_3\text{CN})_2^-$.

The Conformational Behaviour of Methylenecyclohexanes Revisited

Heidi M. Muchall,⁽¹⁾ Petrina R.N. Kanya⁽¹⁾ and Jean Lessard⁽²⁾

(1) Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University, Montréal, (2) Département de Chimie, Université de Sherbrooke, Sherbrooke

Conformational analyses on 2-substituted (methoxy, vinyloxy and acetoxy) methylenecyclohexanes have been performed computationally at HF, B3LYP, PBE0 and MP2 levels with the 6-31G(d) basis set. The global minimum for the methoxy substituent is an axial conformer. For the vinyloxy substituent, except for PBE0, an axial conformer is determined as the global minimum. The acetoxy substituent prefers the equatorial orientation. This sequence is in keeping with the operation of an "unsaturation effect" in addition to an anomeric effect. For a full conformational analysis, torsional potentials for the substituents have been generated, which show further low-energy minima that affect the equilibrium composition. In general, axial conformers dominate the equilibrium. In order to reproduce the experimentally observed predominance of equatorial conformers for vinyloxy and acetoxy substituents, PBE0 has to be employed. CSGT isotropic shielding tensors from B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) have been employed for comparison with experimentally observed ¹³C chemical shifts.

Self-Assembled Alkynyl Thin Films: Theoretical Evaluation and Experimental Fabrication

Adam Dickie, Ashok Kakkar and Tony Whitehead
Department of Chemistry, McGill University, Montréal

Theoretical Evidence for the Catalytic Role of Copper Metal Ions in the Degradation of S-Nitrosothiols

Céline Toubin, David Yeung, Ann M. English and Gilles H. Peslherbe

Centre for Research in Molecular Modeling and Department of Chemistry and Biochemistry, Concordia University, Montréal

The degradation of S-nitrosothiols (RSNOs) to release NO is believed to be catalyzed by CuI ions but the mechanism remains unclear. Kinetic experiments have shown that decomposition rates vary significantly with the chemical nature of the RSNO considered. On the basis of first-principles calculations, the catalytic role of CuI ion is investigated for the decomposition of S-nitrosocysteine and its N-acetylated and ethyl ester derivatives, and for S-nitrosohomocysteine. This preliminary study focuses on the CuI-RSNO intermediates involved in the decomposition pathway. The model chemistry has been validated by comparing calculated CuI-ligand binding energies and S-N bond homolysis energies with available experimental data. Calculations show that the formation of CuI-RSNO intermediates results in weakening of the S-N bond and strengthening of the N-O bond, which would promote S-N bond breaking and NO release from S-nitrosothiols.

Molecular Determinants of Biological Proton Transport

Régis Pomès

Structural Biology and Biochemistry, Hospital for Sick Children, and Department of Biochemistry, University of Toronto, Toronto

The translocation of protons across membranes is one of the most important chemical reactions to occur in biology. In protic solvents and in membrane proteins, long-range proton transport is mediated by a Grothuss relay mechanism involving successive transfers of hydrogen nuclei in extended hydrogen-bonded networks. The physical basis for the movement of H⁺ in ion channels is explored using molecular dynamics simulations. Comparative studies of the hydrogen-bonded water chain (water wire) embedded in native and chemically-modified gramicidin pores reveal the subtle interplay of structural and dynamic properties controlling biological proton translocation and offer a detailed model to understand the molecular origin of selectivity and blockage in other channels, in enzymes, and in pumps.

Improved Hydrogen Adsorption Capacity of Doped-Carbon Nanotube Bundles

P. Guay⁽¹⁾ and A. Rochefort⁽²⁾

(1) INRS Énergie, Matériaux et Télécommunications, (2) École Polytechnique de Montréal, Montréal

The ability of carbon nanostructures to store hydrogen still remains a controversial subject. For example, the reported experimental values for hydrogen uptake in carbon nanotubes vary from 0.4% and 67% wt. In contrast, assuming a physisorption mechanism on graphite planes, most numerical studies agree to give a gravimetric volume of adsorbed hydrogen around 1% wt. at room temperature and 10 MPa. Clearly, in order to explain the large hydrogen uptake obtained experimentally, one has to invoke a different adsorption mechanism than physisorption. The most trivial explanation of large hydrogen uptake in carbon nanotubes is to invoke the participation of residual metallic impurities (Fe, Co, Ni, Ti). Using various carbon nanostructures and with the help of Monte-Carlo simulation techniques, we have studied the effect of heteroatoms within carbon nanotube bundles structure on the final adsorption properties. We will discuss a different hydrogen adsorption mechanism in which the gravimetric volume of adsorbed hydrogen increases by as much as 10% when heteroatoms simulating the presence of metallic impurities are considered.

Computational studies of hydrolysis of N-sulfinyl-compounds

E.V. Ivanova and H.M. Muchall

Centre for Research in Molecular Modeling and Department of Chemistry and Biochemistry, Concordia University, Montréal

N-sulfinyl compounds are widely used in synthetic organic chemistry. Depending on their substituents, these compounds exhibit different chemical behavior, *e.g.* aliphatic N-sulfinylamines are extremely sensitive to hydrolysis, aromatic species are more resistant to water, and N-sulfinylhydrazines are stable in water. Using quantum chemical calculations along with “Atoms in Molecules” (AIM) theory, one can probe reasons for observed reactivities. In this work, we report optimized geometries, conformations, and complexation energy of N-sulfinylaniline and N-sulfinyl-N'-phenylhydrazine with water which were performed at the different levels of theory. AIM theory is used to analyze the hydrogen bonding in these complexes.

Electron Transport into Organized Low-Dimensional Molecular Systems

A. Rochefort^(1,2), M. Layachi^(2,3), R. Martel⁽⁴⁾, Ph. Avouris⁽⁴⁾ and Y. Savaria⁽³⁾

(1) *Département de génie physique and École Polytechnique de Montréal, Montréal* (2) *Centre de recherche en calcul appliqué (CERCA), Groupe Nanostructures, Montréal* (3) *Département de génie électrique, École Polytechnique de Montréal, Montréal* (4) *IBM Research, Yorktown Heights, NY*.

One promising approach to assemble molecules into an active electronic component involves self-assembling monolayer (SAM) techniques. This would ideally lead to the formation of highly packed and organized molecular structures on a metallic template. Once a dense structure is formed, molecular interactions should become significant. We have studied the influence of π -orbital coupling in arenes-based assembly on its resulting electronic and electrical properties. The conduction and the field-switching properties of the assembly are compared as the intermolecular distances are reduced to below 5 Å. We have investigated the electron transport within a single molecule, and more importantly, between the molecules which form a 1D molecular wire. We have also explored different electrode geometries. For this specific arrangement, we predict a large conductance modulation upon application of a transverse gate field, for which the switching mechanism involves a delocalized π -resonance - i.e. resonant tunneling in the intermolecular π - and π^* -bands of the molecular assembly.

Introducing the QM/MM Functionality within the DeFT Software Package and Its Application to Free Energy Calculations

E. Paradis and A. St-Amant

Department of Chemistry, University of Ottawa, Ottawa

We have implemented the QM/MM functionality within the DeFT density functional (DF) software package by interfacing it with AMBER's ROAR module. A 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 others are handled at the simple MM level. We use this QM/MM functionality to optimize a hybrid AM1/DF free energy perturbation scheme. Preliminary results will be presented.

Theoretical Studies of Lithium Hexamethyl Disilazide Complexes: Effects of Solvation and Aggregation

S. Popenova, R. C. Mawhinney and G. Schreckenbach

Department of Chemistry and Biochemistry and Centre for Research in Molecular Modeling, Concordia University, Montréal

Lithium amides are probably most widely used in chemical synthesis as nucleophilic or basic reagents. In solution, lithium amides exist in monomeric, dimeric and higher oligomeric states at the same time. In addition, each of these species usually form solvent complexes. The general formula is $(RR'NLi \cdot xL)_n$, where L is a solvent (usually polar) with x degrees of solvation and each molecule has n degrees of aggregation. Understanding of complexation and aggregation in lithium amides is very important since it impacts on reactivity. A common method for determining lithium amide solvation and aggregation is ^6Li , ^{15}N and ^{13}C NMR spectroscopy. Gathered by many research groups, experimental information on lithium amide structures is often contradictory. Theoretical methods, such as Density Functional Theory, can be used to examine, and resolve these issues. Here we report theoretical predictions for lithium hexamethyl disilazide complexes solvated with THF in different states of aggregation. Results will be presented for molecular geometries, energies and chemical shieldings for systems with the general formula $\{[(\text{Me})_3\text{Si}]_2\text{NLi} \cdot x\text{THF}\}_n$. Future work will be also discussed

Photoresponsive Supramolecular Systems: Self-Assembly of Azodibenzoic acid Linear Tapes and Cyclic Tetramers

F. Rakotonradany, M. A. Whitehead and H. F. Sleiman

Department of Chemistry, McGill University, Montréal

A new strategy to effect photoinduced control over molecular self-assembly is reported. This strategy uses the reversible trans-cis photoisomerization of a novel azobenzene system, where the trans- and cis-forms self-assemble into dramatically different higher-order structures. The trans-azobenzene form of this molecule associates into infinite linear tapes, while the cis-azobenzene form undergoes self-assembly into hydrogen bonded cyclic tetramers. This results in a second-level of association where the cis hydrogen-bonded cycles ultimately form rod-like structures through stacking interactions. The most recent experimental and theoretical results will be reported. Future work will be also discussed.

Calculation of Resonance Energies and Widths of HCO using a Novel Lanczos-based Method

T. Carrington Jr. and J. C. Tremblay

Département de Chimie, Université de Montréal, Montréal

An L2 direct product basis approach is used to calculate resonance state energies and widths of the triatomic molecule HCO. The new method uses a complex absorbing potential (CAP) as a perturbation for the Hamiltonian to damp the amplitude of the outgoing wave function. In order to avoid complex arithmetic, an energy-dependant CAP is used. A particular mapping of the Hamiltonian eigenvalues to the vicinity of the unit disk proposed by Mandelshtam and Neumaier has proved to be very efficient in conjunction with Filter Diagonalization (FD). However, since Lanczos-based methods are at least as reliable as FD and often easier to use, the new method is using this particular approach. Some numerical results will be presented to demonstrate the efficiency of this new method.

Structural Elucidation of Calbindin D_{28K} with Intramolecular Cross-linkers, Mass Spectrometry and Molecular Mechanics

D. Y.-H. Yeung, G. H. Peslherbe and A. M. English

Centre for Research in Molecular Modeling and Department of Chemistry and Biochemistry, Concordia University, Montréal

Conventional methods for the elucidation of the tertiary structure of proteins are NMR spectroscopy and X-ray crystallography. However, these methods have limitations. A recent study suggested the possibility of structural characterization of proteins by the use of sequence alignment, chemical cross-linking and mass spectrometry. We are applying this approach to the characterization of the structure of a calcium binding protein, human calbindin D_{28k}. The structure obtained from these experiments will be modeled using molecular mechanics. The simulations will aid in the design of further experiments, allow us to refine the structure and suggest other conformations that the protein may adopt in both its calcium-free and calcium-loaded forms.

Structure and Spin Relaxation of Rh_n ($n=2-15$) Cluster

M. Zhuang and M. Ernzerhof

Département de Chimie, Université de Montréal., Montréal

We used the spd tight-binding model to study the geometric and magnetic structures of the cluster Rh_n ($n=2-15$). For each cluster, we started with possible structure and randomized the spin on each atom. After self-consistently relaxation, several different configurations for each cluster, both in structure and spin, are obtained. The ground states for Rh clusters are ferromagnetic, in agreement with experimental and other theoretical results. The metastable state with different magnetic moment are found to be close to the ground state in energy. The energy difference is roughly decreasing with the atom number. We also got a noncollinear spin structures for Rh_6 , Rh_{11} and Rh_{12} .

Molecular Vibrational Excitation in Surface-Induced Fragmentation of $(O_2)_m$ and $(N_2)_m$ Clusters

T.-N. V. Nguyen⁽¹⁾, G. H. Peslherbe⁽¹⁾, H. Vach⁽²⁾

1) Centre for Research in Molecular Modeling and Departement of Chemistry and Biochemistry, Concordia University, Montréal, 2) Laboratoire de Physique des Interfaces et des Couches Minces ,Ecole Polytechnique, Palaiseau, France

Recent experimental results show evidence for a completely new oxidation process of silicon surfaces with an $(O_2)_m$ cluster beam . 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”. This interpretation has been tested by an in-depth study of $(N_2)_m$ and $(O_2)_m$ surface scattering, using classical trajectory dynamics. When simulating the collision, it appears that the cluster products are only slightly vibrationally excited. Under the employed experimental conditions, molecular dissociation is not possible since it requires a much higher cluster incident velocity. Furthermore, the cluster size does not catalyze but hinders monomer vibrational excitation, which leads us to suggest the existence of an optimal cluster size for cluster-catalyzed reactions. An alternate reaction path is proposed to explain the experimental findings.

Quantum and Classical Monte Carlo Simulations of $\Gamma(\text{H}_2\text{O})_n$ clusters (n=12, 20)

M. Sbata and G. H. Peslherbe

*Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry
Concordia University, Montréal*

Quantum effects are expected to be significant in low-temperature ionic water clusters, since hydrogen atoms are very 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 a comparison of the structural properties and binding energies of $\Gamma(\text{H}_2\text{O})_n$ (n=12, 20) clusters at 70 K and 300 K using both classical and quantum Monte Carlo simulations with pairwise additive potentials. The quantum simulations employ the Fourier Path Integral Monte Carlo method. The influence of quantum effects on the cluster structural properties and thermodynamics is discussed.

Conformational Studies of Substituted Cyclohexanes

P. R.N. Kanya⁽¹⁾, H. M. Muchall⁽¹⁾ and J. Lessard⁽²⁾

(1) Centre for Research in Molecular Modeling and Department of Chemistry and Biochemistry, Concordia University, Montréal, (2) Département de Chimie, Université de Sherbrooke, Sherbrooke

Previously obtained ¹³C NMR experimental data on 3-substituted cyclohexenes and 2-substituted tetrahydropyrans (substituents being methoxy, acetoxy and vinyloxy groups), showed that both the anomeric and gamma-effects were observed. A computational analysis on the afore mentioned compounds has been completed to confirm the experimental data. The computational study involved obtaining the ¹³C NMR shifts of the optimized compounds. The lowest energy conformers were determined once torsional energy profiles had been created for the compounds.

Water Mobility in Small Aerosol OT Reverse Micelles

M.R. Harpham⁽¹⁾, N.E. Levinger⁽¹⁾, B.M. Ladanyi⁽¹⁾ and K.W. Herwig⁽²⁾
(1) Colorado State University, Fort Collins, (2) ORNL

Reverse micelles are nanoscale droplets of polar solute surrounded by a surfactant layer in nonpolar solvents. We have used quasielastic neutron scattering (QENS) to investigate the mobility of water molecules in small reverse micelles consisting of water/deuterated AOT/perdeuterated isooctane. Water/surfactant ratios of 1, 2.5, and 5 have been investigated using the QENS spectrometer at Argonne National Lab, IPNS division. Computer simulations of reverse micelles of these water/surfactant ratios have been performed and used to predict QENS spectra to further investigate the dynamics of the water molecules and make comparisons to experimental data. Preliminary analysis indicates that the motions of water molecules are slower than in bulk water for the low ratio samples. In addition, the mobility of the water molecules strongly depends on the distance from the interface.

Theoretical Studies of the Photo-Induced Dissociation of Metal Clusters

Y. Wei, P. Larrégaray and G. H. Peslherbe
Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University, Montréal

We present a study of the photo-induced unimolecular dissociation of Al_{13} clusters. The interactions within the cluster are described by two-body and three-body potential terms. Various sets of specific cluster vibrational modes are excited in order to simulate laser photoexcitation. The dissociation dynamics is then followed in time via classical trajectory simulations. A key question in unimolecular reaction theory is whether reactions proceed through rapid intramolecular vibrational energy redistribution (IVR) following excitation, followed by a statistical Rice-Ramsperger-Kassel-Marcus (RRKM) process. Our classical trajectory results suggest that IVR is indeed rapid and that the photo-induced dissociation of Al_{13} is a statistical process, with rate constants essentially insensitive to the set of vibrational modes initially excited. Accordingly, the simulated cluster unimolecular dissociation rate constants are found in good agreement with the predictions of accurate statistical models.

A Theoretical Study of the Ring Contraction of 3-Sila-2-oxacyclohexylidene and 2-Oxacyclohexylidene

P. G. Loncke and G. H. Peslherbe

Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University, Montréal

We have investigated the mechanisms for ring contraction of 3-sila-2-oxacyclohexylidene and 2-oxacyclohexylidene by means of density-functional theory (DFT) calculations and the quantum theory of atoms in molecules (AIM). Pathways involving concerted and step-wise biradical mechanisms were examined. In regards to the concerted mechanistic pathways, ring contraction of 3-sila-2-oxacyclohexylidene appears to occur via nucleophilic attack by the carbene lone pair at silicon whereas ring contraction of 2-oxacyclohexylidene seems to involve an anion-like alkyl shift from oxygen to the “vacant” carbene *p* orbital. Overall, based on the computed thermodynamic data, it appears that ring contraction of 3-sila-2-oxacyclohexylidene occurs via the concerted mechanistic pathway whereas ring contraction of 2-oxacyclohexylidene occurs via the step-wise biradical mechanistic pathway.

Neutron Reflectivity Study of poly(styrene Maleic Anhydride) at the Air Water Interface: Theory and Experiment

C. Malardier-Jugroot, T. van de Ven and M. A. Whitehead

Department of Chemistry, McGill University, Montréal

Photoresponsive Supramolecular Systems: Self-Assembly of Azodibenzoic Acid Linear Tapes and Cyclic Tetramers. Theory and Experiment

F. Rakotondradany, H. Sleiman and M.A. Whitehead
Department of Chemistry, McGill University, Montréal

Stationary States of Model Systems by Damped Bohm Dynamics

J. Smaby and F. G. Amar
Department of Chemistry, University of Maine

We add a damping term to the Bohm dynamics approach of Wyatt (1) in order to find stationary states for model quantum systems. We compare the use of a meshless method with a global fit method to generate the dynamics of the probability density. Results are given for several one dimensional systems and some preliminary results on excited states are presented.

(1) C. L. Loprore and R. E. Wyatt, PRL 82, 5190 (1999).

Polarization Energies of Mixed Xe/Ar Cluster Ions

J. Smaby and F. G. Amar

Department of Chemistry, University of Maine

We calculate the polarization energy of singly ionized mixed rare gas clusters as a function of the position of the ionized atoms. Following Lundwall et. al. (1), we start with a core of about 500 Xe atoms surrounded by approximately 1500 Ar atoms. Shell structure is observed, in qualitative agreement with the experimental results of the Swedish group.

(1) M. Lundwall, M. Tchapyguine, G. Ohrwall, R. Feifel, M. Gisselbrecht, A. Lindgren, S. Sorenson, S. Svensson, and O. Bjorneholm, "Synchrotron Radiation-based Photoelectron Spectroscopy Study of the Radial Segregation in Free Heterogeneous Ar/Xe Clusters", poster B-VII-9 presented at ISSPIC XI, Strasbourg, France, Sept. 9-13, 2002.

Photodissociation Dynamics of HCl. Experimental Data and Modelling of the Superexcited States

C. Romanescu, S. Manzhos, D. Boldovsky and H.-P. Looock

Department of Chemistry, Queen's University, Kingston

The Velocity-Map Imaging was used to record photoelectron and photoion spectra of HCl following excitation to the E 1S+(0+), V 1S+(0+), g 3S-(0+) or F 1D(2) states, to determine the branching ratios between autoionization and (pre)dissociation channels and to measure the anisotropy parameters of the charged particles. Superexcited state potential reconstruction by fitting the HCl+ vibrational spectrum allows us to characterize superexcited states 2.6 -2.9 eV above the first dissociation limit and to compare different autoionization models.

Ionic Dissociation of Molecules in Clusters and on Ice Surfaces

P. Ayotte

Département de chimie, Université de Sherbrooke, Sherbrooke

Molecular Modelling of Poly(ethylene Oxide), Model Cofactors, and their Interactions with Water

R. Gaudreault, T. van de Ven and M.A. Whitehead

Department of Chemistry, McGill University, Montréal

Density Functional Theory Study of Nickel Indenyl Complexes as Catalysts

V. Tessier, M. Ernzerhof and D. Zargarian

Université de Montréal, Montréal

PARTICIPANTS

Francois	Amar	Francois.Amar@unit.maine.edu
Patrick	Ayotte	patrick.ayotte@usherbrooke.ca
Peter	Bird	birp@vax2.concordia.ca
Tucker	Carrington	Tucker.Carrington@umontreal.ca
Christine	DeWolf	cdewolf@alcor.concordia.ca
Adam J.	Dickie	adam.dickie@mail.mcgill.ca
Ann M.	English	english@vax2.concordia.ca
Matthias	Ernzerhof	matthias.ernzerhof@umontreal.ca
Elisa	Fadda	elisa@cerca.umontreal.ca
Roger	Gaudreault	Rgaudreault@cascades.com
Patrice	Guay	patrice.guay@nanotechnologies.qc.ca
Mike R.	Harpham	Mharpham@lamar.colostate.edu
Sean R.	Hughes	sean@cermm.concordia.ca
Elena V.	Ivanova	Elena@cermm.concordia.ca
Petrina	Kamya	kpetrina2@yahoo.com
Denise M.	Koch	denise@cermm.concordia.ca
Mohammed	Layachi	Mohammed.layachi@polymtl.ca
Paul G.	Loncke	paul@cermm.concordia.ca
Hans-Peter	Loock	hploock@chem.queensu.ca
Sergei V.	Manzhos	Manzhos@chem.queensu.ca
Robert C.	Mawhinney	rmahwinn@alcor.concordia.ca
Philippe G.	Merle	pgmerle@alcor.concordia.ca
Heidi M.	Muchall	muchall@alcor.concordia.ca
Tao-Nhan	Nguyen	nhan@cermm.concordia.ca
Etienne	Paradis	eparadis@sympatico.ca
Gilles H.	Peslherbe	ghp@alcor.concordia.ca
Regis	Pomes	pomes@sickkids.on.ca
Svetlana G.	Popenova	popenova@alcor.concordia.ca
Felaniaina	Rakotondradany	felaniaina.rakotondradany@mail.mcgill.ca
Alain	Rocheffort	alain.rocheffort@polymtl.ca
Constantin	Romanescu	Romanescu@chem.queensu.ca
Andrew B.	Ryzhkov	Andrew@Zephyr.Meteo.McGill.Ca
Mouna	Sbata	mouna@cermm.concordia.ca
Armand	Soldera	Armand.Soldera@Usherbrooke.ca
Qadir K.	Timerghazin	Qadir@cermm.concordia.ca
Jean Christophe	Tremblay	jc.tremblay@umontreal.ca
Xiaogang	Wang	xiaogang.wang@umontreal.ca
Yin	Wei	Yin@cermm.concordia.ca
Tony	Whitehead	tony@maw.chem.mcgill.ca
David Y.-H.	Yeung	david@cermm.concordia.ca
Min	Zhuang	moin.zhuang@umontreal.ca
Tom	Ziegler	ziegler@ucalgary.ca