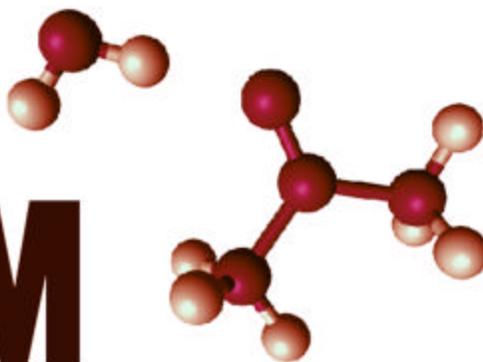


CERMM



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

First Annual Symposium

Program & Book of Abstracts

Monday, January 22, 2001 – 8:30 am to 12:30 pm

De Sève Theatre, McConnell Building, Concordia University
1400 De Maisonneuve Blvd. West, Metro Guy-Concordia

Sponsors

Faculty of Arts and Science, Concordia University
Department of Chemistry and Biochemistry, Concordia University



Concordia
UNIVERSITY

Real education for the real world

Program

- 8:30 Opening Address - Dr. Gilles Peslherbe, CERMM Director
Dr. Martin Singer, Dean, Faculty of Arts & Science, Concordia University
Dr. Marcus Lawrence, Chair, Department of Chemistry and Biochemistry
- 9:00 Plenary Lecture - Prof. James T. Hynes (U of Colorado and ENS)
New Theoretical Insights for Excited Electronic State Proton Transfers in Solution
- 9:55 Coffee Break
Research presentations - Chair: Dr. Heidi Muchall
- 10:10 Alexei Khalizov and Parisa Ariya, *A Theoretical Study on the Role of Halogens and Halogen Oxides in Tropospheric S(IV) Oxidation*
- 10:20 Balakrishnan Viswanathan and Parisa Ariya, *Theoretical Investigation of Hg⁰ Reactions with X/X₂/OX Species*
- 10:30 Elham Ghobadi and John Capobianco, *Crystal Properties of Alpha Quartz GeO₂*
- 10:40 Andrea Romeo, John Capobianco and Ann English, *Biological Mechanisms of S-Nitrosation*
- 10:50 Ngoc-Thanh Vu and David Jack, *Structures and Phase Transitions of CO Adsorbed on Ionic Substrates*
- 11:00 Abdulwahab Sallabi and David Jack, *Nonuniversal Critical Exponents in Monolayer Nitrogen*
- 11:10 Denise Koch and Gilles Peslherbe, *On the Photochemistry of Glyoxal*
- 11:20 Tao-Nhan Nguyen and Gilles Peslherbe, *Ionic Microsolvation in Acetonitrile and Water Clusters*
- 11:30 Cyril Puel and Gilles Peslherbe, *On the Regioselectivity of Nitrilimine Cycloadditions*
- 11:40 Paul Loncke and Gilles Peslherbe, *Mechanisms of Intramolecular Siloxycarbene Rearrangements*
- 11:50 Qadir Timerghazin and Gilles Peslherbe, *On the Role of Solvation in Photochemistry: Charge Transfer To Solvent in Photoexcited Ionic Clusters*
- 12:00 Sean Hughes, Tao-Nhan Nguyen, John Capobianco and Gilles Peslherbe, *Spectroscopy of Lanthanide Ions in Complex Environments*
- 12:10 Jaffer Hasnain, Ann English and Gilles Peslherbe, *Probing Peptide-Denaturant Interactions*
- 12:20 Joseph Patapas and Heidi Muchall, *Photolytic Deprotection of Ketones from Aromatic Hydrazones*
- 12:30 Closing - Dr. Ann English
Lunch buffet and informal discussions - McLeans Pub, 1210 Peel St.
- 15:30 End of Symposium

Abstracts

Plenary Lecture

New Theoretical Insights for Excited Electronic State Proton Transfers in Solution

James T. Hynes

Département de Chimie

Ecole Normale Supérieure, Paris, FRANCE

& Department of Chemistry and Biochemistry

University of Colorado, Boulder, USA

Excited electronic state proton transfer (ESPT) reactions in solution have been an important photochemical reaction class for many years, an aspect accelerated more recently via the application of ultrafast spectroscopic methods. Yet it cannot be claimed that these reactions are understood from a fundamental molecular perspective. In this talk, we will briefly recount some of the highlights of our recent theoretical work, addressed to ultimately providing such an understanding, informed by experimental results on hydroxyarene systems from the group of T.-H. Tran-Thi in Saclay. We will focus, in the context of intermolecular proton transfer to a water solvent molecule, on the following issues:

- 1) What is the reaction coordinate determining the activation free energy? We will argue that, when due account is taken of the quantum mechanical character of the proton motion, the reaction coordinate is largely determined by the solvent, and is not the proton coordinate itself [1].
- 2) How many elementary steps are involved in the ESPT reaction as studied via ultrafast spectroscopy? We will argue that in general there are likely to be three, whose nature will be described [2].
- 3) What is the fundamental cause of the greatly increased acidity in ESPT reactions compared to the ground state analogues? We will argue that it is not due to an initial charge transfer in the Franck-Condon absorption of the ground state acid--as in one traditional view--but rather arises from electronic effects in the excited state anionic product of the ESPT reaction [3].

Our collaborators in this work are indicated in the references.

[1] For discussion of these issues for ground electronic state proton transfer, see K. Ando and J.T. Hynes, *J.Phys. Chem. A*, **103**, 10398 (1999).

[2] T.-H. Tran-Thi, T. Gustavsson, C. Prayer, S. Pommeret and J.T. Hynes, 'Primary Ultrafast Events Preceding the Photoinduced Proton Transfer from Pyranine to Water', *Chem. Phys. Lett.*, in press; T.-H. Tran-Thi, C. Prayer, P. Millie, P. Uznanski, and J. T. Hynes, "Effect of Sulfonate Groups and Solvents on the Nature of the Transitions of Pyrenol and Pyranine. Identification of an Intermediate in the ESPT Reaction", sub. for publication; C. Prayer, T.H.Tran-Thi and T. Gustavsson, *AIP Conference Proceedings* 364, ed. A. Tramer (AIP, New York, 1995). p. 333.

[3] G. Granucci, J. T. Hynes, P. Millie, T.-H. Tran-Thi, "A Theoretical Investigation of Excited State Acidity of Phenol and Cyanophenols", *J. Am. Chem. Soc.*, in press.

A Theoretical Study on the Role of Halogens and Halogen Oxides in Tropospheric S(IV) Oxidation

Alexei Khalizov and Parisa Ariya

Department of Chemistry and Department of Atmospheric and Oceanic Sciences
McGill University

To evaluate the role of halogens and halogen oxides in the oxidation of S(IV) in the troposphere, we performed a theoretical investigation of their reactions with SO₂. Using very extended basis sets for correlated ab initio calculations was shown to be necessary to describe the energetics correctly, while computationally inexpensive B3LYP provides reliable data even with medium size basis sets. The ClSO₂ radical was found to be stable enough to provide oxidation of atmospheric SO₂ via the reaction with atomic chlorine, while reaction with Br is unimportant. At the same time, contribution from BrO is expected to be significantly larger than from ClO and Cl. The implications of these data on direct or indirect overall rate of S(IV) to S(VI) will be discussed.

Theoretical Investigation of Hg⁰ Reactions with X/X₂/OX Species

Balakrishnan Viswanathan and Parisa Ariya

Department of Chemistry and Department of Atmospheric and Oceanic Sciences
McGill University

The lifetime of total gaseous mercury (TGM) in the atmosphere, comprised mainly of Hg⁰ (~90 %) is estimated to be of the order of 1-2 years. Recent measurements of TGM in surface air at Alert, NWT show a recurring annual pattern with frequent episodes of exceedingly low values in spring time. Lack of kinetic data regarding mercury reactions prevents an explanation of these unusual events. Theoretical calculations have been carried out to investigate the thermodynamics and kinetics of the reactions of Hg⁰ with Cl, Br, ClO, and BrO radicals. Difficulties experienced during the studies and data obtained will be briefly discussed in light of the current concerns.

Crystal Properties of Alpha Quartz GeO₂

Elham Ghobadi and John Capobianco
Department of Chemistry and Biochemistry
Concordia University

The α -quartz type GeO₂ crystal was simulated using the Buckingham model potential including the shell model and bond bending terms. The electrostatic potential was evaluated by the use of the Ewald method. Constant pressure minimization with simultaneous fitting was used to determine the interatomic potential parameters. The validity of the model potential was tested by calculation of dielectric and elastic data, thermodynamic properties, phonon dispersion curves, phonon density of states, and infrared phonon intensities. Calculated properties compare well with the experimental data reported in the literature.

Biological Mechanisms of S-Nitrosation

Andrea Romeo, John Capobianco and Ann English
Department of Chemistry and Biochemistry
Concordia University

There is evidence that binding of the vasorelaxant, nitric oxide (NO), to Cys β 93 of hemoglobin (Hb) plays a role in blood pressure regulation. NO reportedly equilibrated between Hb and low-molecular-weight nitrosothiols such as nitrosoglutathione (GSNO) via *trans*-S-nitrosation (NO⁺ transfer between thiols). S-Nitrosation of Cys β 93 was directly probed by FTIR by monitoring the ν (SH) vibrations of Hb and by ESI-MS. The results indicate that Cys β 93 is S-nitrosated when oxyHb (but not deoxyHb) is exposed to GSNO (1:1 heme/GSNO). No FTIR nor ESI-MS evidence was obtained for oxyHb S-nitrosation in the presence of DTPA, a Cu^{II} chelator. Monitoring the heme Soret and visible bands revealed that oxyHb was converted to metHb in the presence of GSNO and that this was inhibited on addition of neocuprin, a Cu^I chelator. The combined data are consistent with a mechanism involving Cu^{II}-catalysis of Cys β 93 S-nitrosation by *free* NO generated by Cu^I-catalysis of GSNO breakdown. The results are inconsistent with simple *trans*-S-nitrosation which is *not* metal catalyzed.

Structure and Phase Transition of CO Adsorbed on Ionic Substrate

Ngoc-Thanh Vu and David Jack
Department of Chemistry and Biochemistry
Concordia University

We have studied the order-disorder phase transition of a carbon monoxide monolayer adsorbed on a sodium chloride substrate using the Metropolis Monte Carlo method. The simulations have been performed in the temperature range from 5K to 60K. At low temperature the system forms ordered phase, which disorders as the temperature is increased. The transition temperature (T_c) is between 30K and 35K. Below T_c , the monolayer has an ordered $p(2 \times 1)$ type structure with correlated azimuthal orientations. Above T_c , the structure undergoes a phase transition to a disordered $p(1 \times 1)$ type phase due to a loss of azimuthal order in the surface plane. Preliminary results of a quantitative analysis, plot of energy profile and heat capacity as a function of temperature, also support the above observed phase transition.

Nonuniversal Critical Exponents in Monolayer Nitrogen

Abdulwahab Sallabi and David Jack
Department of Physics
Concordia University

Monolayer nitrogen adsorbed on the NaCl(001) surface is used to test the validity of the theory of critical phenomena and its applicability to molecular systems. Monte Carlo simulations predict that this system undergoes a continuous order-disorder transition near 25 K. The values of the critical exponents are calculated and found to deviate significantly from the Ising values. It is shown that this system falls into the same universality class as the XY model with cubic anisotropy where the exponents are “nonuniversal.”

On the Photochemistry of Glyoxal

Denise Koch and Gilles Peslherbe
Department of Chemistry and Biochemistry
Concordia University

Glyoxal ($C_2H_2O_2$) unimolecular dissociation has been the subject of many experimental and theoretical studies and some questions remain regarding the predominant pathway for dissociation. Molecular beam photodissociation studies identify the major pathway as that which leads to the formation of formaldehyde (CH_2O) and carbon monoxide (CO). Thermal decomposition experiments and theoretical studies, on the other hand, predict the *triple whammy* pathway that leads directly to $H_2 + 2CO$ to be predominant. The objective of the work presented here is to elucidate these discrepancies by performing a thorough *ab initio* exploration of the glyoxal free energy surface.

Microsolvation of Alkali and Halide Ions in Acetonitrile and Water Clusters

Tao-Nhan Nguyen and Gilles Peslherbe
Department of Chemistry and Biochemistry
Concordia University

We present a theoretical study of ionic microsolvation in acetonitrile and water clusters. Structural properties are extracted from room-temperature Monte Carlo simulations performed with model potentials. The potential functions are derived from experimental data supplemented with quantum chemistry data for small clusters. Similarities and differences in the solvation properties of the Na^+ , Cs^+ and I^- ions in acetonitrile and water clusters are then discussed. A remarkable result that we will discuss in particular is that large halide ions tend to adopt a well-defined interior solvation structure in acetonitrile, while they tend to sit at the surface of the solvent network in water clusters.

On the Regioselectivity of Nitrilimine Cycloadditions

Cyril Puel and Gilles Peslherbe
Department of Chemistry and Biochemistry
Concordia University

A combination of quantum chemistry and frontier molecular orbital theory is used to investigate the regioselectivity of nitrilimine cycloaddition with alkenes. Reported experimental and (low-level) theoretical studies seem to show some discrepancies about the regioselectivity of these reactions. Different substituted nitrilimines are thus studied in order to infer their cycloaddition reaction mechanism and determine whether substituents play a major role in the regioselectivity of the reaction. Another point of interest lies in the actual electronic structure of nitrilimines. For example, the calculated charge distributions and molecular geometries of unsubstituted nitrilimines differ from those one would expect on the basis of their commonly accepted valence-bond structures. The sensitivity of our findings with respect to the choice of model chemistry is also discussed.

Mechanisms of Intramolecular Siloxycarbene Rearrangements

Paul Loncke and Gilles Peslherbe
Department of Chemistry and Biochemistry
Concordia University

Recent experimental studies have provided evidence that methoxy(triphenylsiloxy)carbene undergoes 1,2-triphenylsilyl migration from oxygen to the carbene centre and decarbonylation affording methyl triphenylsilyl formate and methyl triphenylsilyl ether respectively. We have performed *ab initio* and density functional theory calculations on the model compound methoxysiloxycarbene, to gain insight into the mechanisms of these intramolecular rearrangements. Our calculations suggest that 1,2-silyl migration involves nucleophilic attack by the carbene lone pair at silicon, while decarbonylation occurs via nucleophilic attack by the methoxy oxygen at silicon. An alternative pathway for decarbonylation was also found, which involves initial formation of methyl silylformate followed by an intramolecular Brook ester rearrangement.

On the Role of Solvation in Photochemistry: Charge Transfer to Solvent in Photoexcited Ionic Clusters

Qadir Timerghazin and Gilles Peslherbe
Department of Chemistry and Biochemistry
Concordia University

Excited states of clusters containing an iodide ion and a few solvent molecules have recently been observed experimentally and are thought to be precursors of the well-known charge-transfer-to-solvent states in bulk solvents. In this work, we have characterized these cluster excited states by means of quantum chemical calculations (Configuration Interaction, Time-Dependent DFT, Complete Active Space SCF). Vertical detachment energies, detachment and attachment electron densities, and charge flow between the ground and excited state cluster structures have been analyzed. In the case of iodide-acetonitrile complexes, the excited state seems to involve the binding of an electron to the dipolar solvent molecule, while the situation seems to be a bit more obscure for acetone and water clusters. The time-dependent DFT method is shown to be a very efficient tool for the prediction of reliable vertical excitation energies in the clusters studied here.

Spectroscopy of Lanthanide Ions in Complex Environments

Sean Hughes, Tao-Nhan Nguyen, John Capobianco and Gilles Peslherbe
Department of Chemistry and Biochemistry
Concordia University

In recent years, there has been a mounting interest in the use of lanthanide ions for many applications in inorganic solid-state chemistry and biotechnology. The aim of this work is to model the spectroscopy of lanthanide ions in diverse environments, such as solvent clusters, aqueous solutions of bio-organic ligands, and sol-gels. We are currently developing a model potential based solely on ab initio data in order to predict the coordination properties of lanthanide ions. Preliminary results for europium-water complexes suggest that higher-order multipole terms need to be included in model potentials in order to properly reproduce ab initio properties.

Probing Peptide-Denaturant Interactions

Jaffer Hasnain, Ann English and Gilles Peslherbe
Department of Chemistry and Biochemistry
Concordia University

FT-IR spectroscopy and molecular modeling are used to probe the interaction between Poly-L- Lysine (PLL), a polypeptide molecule, and Guanidine Hydrochloride (GdnHCl), a chemical denaturant. Preliminary analysis of the spectra suggests that GdnHCl interacts with the side chain of PLL while the polypeptide backbone remains unaffected. Further studies will be discussed, which combine FT-IR spectroscopy and molecular modeling in order to confirm this proposed molecular mechanism. We anticipate that this work will bring some insight into the mechanism of protein folding.

Photolytic Deprotection of Ketones from Aromatic Hydrazones

Joseph Patapas and Heidi Muchall
Department of Chemistry and Biochemistry
Concordia University

An important topic in synthetic organic chemistry is the clean and efficient protection/deprotection of functional groups. Our work focuses on ketones and their photolytic deprotection from tosylhydrazones. We find that, in the presence of chloranil, irradiation of a tosylhydrazone with UV light generates a ketone quickly and in quantitative yields. Current work primarily focuses on the mechanism and two aspects will be discussed. First, the source of oxygen in the regenerated ketone, which we probe experimentally, and second, the role of a hydrazone radical cation generated through oxidation by chloranil. Computational studies will be carried out to determine several aspects, including the site of oxidation, the change in geometry upon oxidation, and the possible fragmentation of the N-N bond on the radical cation.