

Second Annual CERMM Symposium

Saturday – January 19th, 2002

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
Sigmawave Informatique



Morning Session

- 8:30 **Registration**
- 8:50 **Opening – Martin Singer, Dean of Arts & Science, Concordia University**
Gilles H. Peslherbe, Director, Centre for Research in Molecular Modeling
- 9:00 **Russell Boyd (Department of Chemistry, Dalhousie University)**
The Development of Computational Chemistry in Canada
- 9:45 **Coffee Break**

Session Chair: Heidi M. Muchall

- 10:15 **Dennis R. Salahub (Steacie Institute for Molecular Sciences, National Research Council)**
Quantum Mechanics and Molecular Mechanics for Hydrogen Bonds
- 10:45 **H. Georg Schreckenbach (Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University)**
Density Functional Calculations of Actinide Complexes
- 11:15 **John S. Tse, D.D. Klug, Z.Q. Li and H. Tutuncu (Theory and Computation Program Steacie Institute for Molecular Sciences, National Research Council)**
Simulation and Rational Design of Materials with Novel Properties
- 11:45 **David Jack (Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University)**
Simulations of Molecules at Solid Surfaces
- 12:15 **Lunch – McKibbins' Pub**

Afternoon Session

Session Chair: Ann M. English

- 14:00 **Adam J. Dickie, Ashok K. Kakkar and M.A. Whitehead (Department of Chemistry, McGill University)**
Molecular Modelling of Self-Assembled Alkynyl Thin Films: Calculation of Symmetry Units
- 14:20 **Alexei F. Khalizov, Balakrishnan Viswanathan, Alexios Gidas and Parisa A. Ariya (Departments of Chemistry and Atmospheric & Oceanic Sciences, McGill University; Department of Chemistry, Dalhousie University)**
Reactions of Gaseous Mercury with Atomic and Molecular Halogens: Theoretical and Experimental Studies and Atmospheric Implications.
- 14:40 **Denise M. Koch, Nihed Châabane, Holger Vach and Gilles H. Peslherbe (Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry,**

Concordia University; Laboratoire de Physique des Interfaces et des Couches Minces, Ecole Polytechnique - France)

Mechanisms of Translational and Rotational Energy Transfer in $(N_2)_n$ Cluster-Surface Scattering

15:00 **Steeve Chrétien and Dennis R. Salahub (Département de chimie, Université de Montréal; Steacie Institute for Molecular Sciences, National Research Council, Ottawa)**
DFT study of the formation of benzene from acetylene on iron clusters, Fe_n ($n=1-4$)

15:20 **Xiao-Gang Wang and Tucker Carrington Jr. (Département de chimie, Université de Montréal)**
A Six-Dimensional Variational Calculation of the Bending Energy Levels of the HF Trimer and DF Trimer

15:40 **Oadir K. Timerghazin, Tao-Nhan Nguyen, and Gilles H. Peslherbe (Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University)**
Theoretical Investigation of Charge Transfer to Solvent in Photoexcited $\Gamma(CH_3CN)_n$ Clusters

16:00 **Break**

16:15 **M.A. Whitehead (Department of Chemistry, McGill University)**
St. Hilaire, the Idea, the Place, the People and the Success

Poster session (17:00 -19:30)

- 1) **Francis Esmonde-White and Heidi M. Muchall (Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University)**
Investigation of a Possible Mechanism for the Formation of a Cyclotrisilene
- 2) **Elisa Fadda, Mark E. Casida and Dennis R. Salahub (Département de chimie, Université de Montréal; Laboratoire d'Etudes Dynamiques et Structurales de la Sélectivité, Université Joseph Fourier (Grenoble I) - France; Steacie Institute for Molecular Sciences, National Research Council, Ottawa)**
Rigorous Justification for Sum-Over-States Density-Functional Perturbation Theory within the Framework of Time-Dependent Density-Functional Theory: The "Loc.3" Approximation for the Calculation of NMR Shielding Parameters
- 3) **Roger Gaudreault, Theo G. M. van de Ven and Michael A. Whitehead (Department of Chemistry, McGill University)**
*Molecular Modelling of Poly(Ethylene Oxide) Model Cofactors; 1,3,6-tri-*o*-galloyl- β -D-glucose and Corilagin.*
- 4) **Hasnain Gulam, Gilles H. Peslherbe and Ann M. English (Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University, Montreal)**
Does Guanidine Hydrochloride Interact with a Polypeptide Backbone ?

- 5) **Sean R. Hughes, John A. Capobianco and Gilles H. Peslherbe** (Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University)
On the Nature of Bonding Interactions in Small Metal Ion-Water Clusters
- 6) **Denise M. Koch and Gilles H. Peslherbe** (Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University)
Thermodynamics of Surface vs. Interior Solvation in Halide-Water Clusters
- 7) **P. Larrégaray, L. Bonnet and J.-C. Rayez** (Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University; Laboratoire de Physico-chimie Moléculaire, Université de Bordeaux I - France)
Rationale for Reagent Reorientation in a Triatomic Bimolecular Collision: The Linear Transformation Model
- 8) **Paul Loncke and Gilles Peslherbe** (Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University)
A Theoretical Investigation of 1,2-Migrations in Methoxysiloxycarbene
- 9) **Cecile Malardier-Jugroot, Theo G. M. van de Ven and Michael A. Whitehead** (Department of Chemistry, McGill University)
Conformation and Interactions of Poly(styrene maleic anhydride) Chains in Water
- 10) **Pratibha Malla and Heidi M. Muchall** (Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University)
Computational Studies of N-Phenyl-N-Sulfinylhydrazines
- 11) **Seongho Moon, Serguei Patchkovskii and Dennis R. Salahub** (Département de chimie, Université de Montréal; Steacie Institute for Molecular Sciences, National Research Council, Ottawa)
Quantum Mechanical Approaches for Paramagnetic NMR Shifts in Density Functional Theory
- 12) **Tao-Nhan Nguyen, Holger Vach and Gilles H. Peslherbe** (Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University)
Molecular Vibrational Excitation in Surface-Induced Fragmentation of $(N_2)_n$ and $(O_2)_n$ clusters.
- 13) **Serguei Patchkovskii and Tom Ziegler** (Steacie Institute for Molecular Sciences, National Research Council, Ottawa; Department of Chemistry, University of Calgary)
Improving "Difficult" Reaction Barriers with Self-Interaction Corrected DFT
- 14) **Cyril Puel and Gilles H. Peslherbe** (Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University)
On the Regioselectivity of Nitrilimine Cycloadditions
- 15) **F. Rakotondradany, M.A. Whitehead and H. Sleiman** (Department of Chemistry, McGill University)
A Theoretical and Experimental Study of Photoswitching Hydrogen-bonded Azodibenzoic Acids

- 16) **Andrew Ryzhkov, Parisa Ariya and Henry Leighton (Department of Atmospheric & Oceanic Sciences, McGill University)**
A Theoretical Study of the Atmospheric Reaction of Carbonyl Oxide with Water Vapor.
- 17) **K. Sallabi and D. B. Jack (Centre for Research in Molecular Modeling, Department of Physics and Department of Chemistry & Biochemistry, Concordia University)**
Structures and Stability of CO and N₂ Physisorbed on MgO: Descending the Devil's Staircase
- 18) **Céline Toubin, David Y.-H. Yeung, Ann M. English and Gilles H. Peslherbe (Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University)**
Theoretical Evidence for the Catalytic Role of Metal Copper Ions in the Degradation of S-nitrosothiols.
- 19) **X. F. Wang, P. Vasilopoulos and F. M. Peeters (Centre for Research in Molecular Modeling and Department of Physics, Concordia University; Departement Natuurkunde, Universiteit Antwerpen - Belgium)**
Spin-current Modulation and Square-Wave Transmission Through Periodically Stuffed Electron Waveguides
- 20) **John Wright and Ann M. English (Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University)**
Mass Spectrometric Protein-based Radical Spin Probing.
- 21) **David Yong-Hoi Yeung, Ann M. English and Gilles H. Peslherbe (Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University)**
Structural Determination of Calbindin-D_{28K} using Intramolecular Cross-linkers, Mass Spectrometry and Molecular Mechanics.

Talks

T1 – 9:00

The Development of Computational Chemistry in Canada

Russell J. Boyd

*Department of Chemistry
Dalhousie University
Halifax, Nova Scotia B3H 4J3*

The development of computational and theoretical chemistry in Canada will be summarized with the focus on the period 1954 to 1997. Headings such as, In the Beginning There Was Quantum Chemistry and Spectroscopy, Expo 67 and Fullerenes, Family Trees and Trends, and Spreading Their Wings, will be used to describe some of the events and personalities that contributed to building a strong cohort of computational chemists in Canada. Some statistical data and trends with respect to academic appointments will be presented. It will be shown that from its relatively late start in the 1950s to its position of pre-eminence in the 1990s, computational chemistry has emerged as one of Canada's strongest disciplines. It can be argued that the recent achievements of Canada's computational and theoretical chemists has contributed significantly to the high impact of Canadian chemistry relative to all other physical science and engineering disciplines. Even greater achievements can be expected from the excellent group of computational chemists that have been hired by Canadian universities during the past decade or so.

T2 – 10:15

Quantum Mechanics and Molecular Mechanics for Hydrogen Bonds

Dennis Salahub

*Steacie Institute for Molecular Sciences,
National Research Council Canada
Ottawa, Ontario, Canada K1A 0R6*

The lecture will center on the structure, energetics and dynamics of systems containing hydrogen bonds. In order to take account of complex environments, whether one is studying reactions on ice, in water, or in biology one needs to consider models that go beyond the practical limits of quantum chemistry, on the one hand, and molecular dynamics, on the other. Hybrid, so-called QM/MM (Quantum mechanics/Molecular Mechanics), methods are being developed. I will present an overview of Density Functional Theory to demonstrate the performance of different functionals in the context of a variety of hydrogen-bonded systems. At the present time the "meta-GGA" functionals which involve the Laplacian of the density and the kinetic energy density represent the state of the art. The importance of polarization effects will be brought out and I will discuss some molecular mechanical methods that take these into account. The question of efficient sampling during simulations will be discussed using the example of formamide-water to illustrate a hybrid approach in which two Markov chains are used, one using quantum mechanics (DFT) to calculate accurate energies and a second one based on a rapid evaluation using polarized molecular mechanics to guide the sampling.

T3 – 10:45

Density Functional Calculations of Actinide Complexes

H. Georg Schreckenbach,

Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University, 1455 de Maisonneuve Blvd. West, Montréal, Québec, Canada, H3G 1M8

We present some results of theoretical studies on complexes of the early actinide elements (U, Np, Pu). Our calculations are based on relativistic density functional theory (DFT). We show results for species that have been observed in aqueous solution (for instance actinyl water complexes, $[\text{AnO}_2(\text{H}_2\text{O})_n]^{1+/2+}$, $n = 4, 5, 6$). We will discuss the extension of previously developed DFT methods for the calculation of NMR chemical shifts to the actinide elements, thus making such methods available for the entire periodic table. Experimentally unknown ^{235}U NMR shieldings (chemical shifts) have been predicted. We find a rather large chemical shift range for this nucleus.

T4 – 11:15

Simulation and Rational Design of Materials with Novel Properties

J.S. Tse, D.D. Klug, Z.Q. Li and H. Tutuncu

*Theory and Computation Program
Steacie Institute for Molecular Sciences, National Research Council of Canada
Ottawa, Ontario, Canada K1A 0R6*

A brief overview of various theoretical techniques in the modeling of materials properties employed at our research program will be presented. These techniques, based on first-principles density functional theory, are applied to the prediction of structural stabilities, physical and transport properties, molecular dynamics and vibrational spectra of extended systems. We will illustrate applications of these techniques with selected examples.

T5 – 11:45

Simulations of Molecules at Solid Surfaces

O. Bitton, J. Dawoud, A. Jakalian, A. K. Sallabi, N.-T. Vu,
and D. B. Jack

Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry and Department of Physics, Concordia University, 1455 de Maisonneuve Blvd. West, Montréal, Québec, Canada, H3G 1M8

An overview of Monte Carlo and Molecular Dynamics studies done on the structures, stability and phase transitions in molecular layers adsorbed on solid surfaces will be presented. A variety of molecule-solid systems and phenomena will be discussed, including the devil's staircase, order-disorder phase transitions, and self-assembled monolayers. The correspondence with experimental results will be discussed as well some of the techniques used.

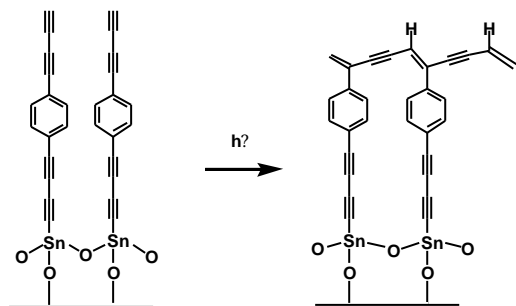
T6 – 14:00

Topochemical Polymerization on Functionalized Tin-Alkynyl Thin Films: Experimental and Theoretical Investigations

Adam J. Dickie, Ashok K. Kakkar, and M.A. Whitehead

*Department of Chemistry, McGill University,
801, Sherbrooke Street West, Montreal, Quebec,
Canada, H3A 2K6.*

The acid-base hydrolysis of aminostannanes with aromatic chromophores terminated by dialkynyl groups creates well-ordered and densely packed thin films on Si(100)/SiO₂ substrates. Exposing the functionalized thin film to UV radiation causes photopolymerization of the diacetylene groups; however, the extent of polymerization is critically dependent on the intermolecular separations within the self-assembled monolayer. This experimental method can lead to the creation of semiconductor surfaces with new electrical and optical properties if the packing and orientation of the molecular film can be understood and optimized. Accessible orientations of the aromatic monolayers are identified through Molecular Mechanics (MM) and semi-empirical PM3 calculations. Rigid van der Waals energy scans, constrained periodic geometry optimizations, and periodic surface simulations are used to determine the close-packed unit cells and the possible polymerized structures.



T7 – 14:20

Reactions of Gaseous Mercury with Atomic and Molecular Halogens: Theoretical and Experimental Studies and Atmospheric Implications

Alexei F. Khalizov,* Balakrishnan Viswanathan,** Alexios Gidas,
Parisa A. Ariya*

* *Departments of Chemistry and Atmospheric and Oceanic Sciences, McGill
University, 801 Sherbrooke St. W., Montreal, PQ, CANADA, H3A 2K6*

** *Department of Chemistry, Dalhousie University, Halifax, Nova Scotia Canada*

Rapid depletion of atmospheric mercury (Hg) and ozone coinciding with high halogens concentrations have recently been observed in Arctic and sub-Arctic. To understand the role of halogen reactions in mercury transformation, we performed complementary theoretical and experimental studies on the reaction of mercury with halogens and halogen oxides. Theoretical calculations were carried out at B3LYP, PW91 and correlated CCSD(T)//QCISD levels of theory using LanL2DZ and mixed basis sets. Ab initio methods were found to be superior to DFT in reproducing geometrical parameters and vibrational frequencies of species involved in reactions between Hg and X/X₂ (X = F, Cl, and Br) as well as in reproducing the reaction enthalpies. The same theoretical procedures gave rise to spurious results when applied to the Hg + XO system. The possible reasons for the discrepancies, including inadequate description of the Hg-O bond, were explored. Experimental kinetic and product studies of the reactions of gaseous Hg with molecular and atomic halogens (X/X₂ where X = Cl, Br) were carried out at atmospheric pressure and room temperature in air and nitrogen. Reaction kinetics was studied using relative and absolute techniques by cold vapour AAS and GC-MS. The measured rate constants for reactions of Hg with Cl₂, Cl, Br₂, and Br were found to be 2.6E-18, 1.0E-11, < 0.9E-16, and 3.2E-12 cm³ molecule⁻¹ s⁻¹, respectively. Wall surface and reaction products strongly accelerate the rate of reaction of molecular halogens with mercury, but practically do not affect the reactions of atomic halogens. The major products found (80 – 90%) were HgCl₂ and HgBr₂ adsorbed on the wall. Non-volatile, non-soluble Hg₂Cl₂, Hg₂Br₂, and HgO might represent the rest of the products. The contribution of aerosols to the reaction products was found to be negligible. On the base of kinetic data and observed concentrations of halogen species we may conclude that only Br atoms are likely candidates to explain the rapid depletions of mercury in the Arctic. Particular attention is to be placed on identified products formed as the results of halogen-initiated reactions of elemental mercury, as they are more soluble than elemental mercury, and hence may be subject to bio-accumulation.

T8 – 14:40

Mechanisms of Translational and Rotational Energy Transfer in $(N_2)_n$ Cluster-Surface Scattering

Denise M. Koch and Gilles H. Peslherbe

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Nihed Châabane and Holger Vach

Centre for Research in Molecular Modeling, Concordia University, and Laboratoire de Physique des Interfaces et des Couches Minces C.N.R.S. - Ecole Polytechnique, 91128 Palaiseau, France

Molecular dynamics simulations were employed to investigate the dynamics of surface-induced $(N_2)_n$ cluster fragmentation. The calculated translational and rotational state distributions of the monomer products of $(N_2)_n$ clusters scattered off a hard surface indicate that the translational states follow a single Maxwell-Boltzmann distribution whereas the rotational state distributions are represented by a sum of two distinct Boltzmann distributions, in agreement with previous experimental findings obtained with a graphite surface. Analysis of the scattering dynamics provide insights into a molecular-level explanation for the differing behaviors of energy transfer to the translational and rotational modes of the monomer products. Our simulation results indicate that translational excitation of scattered products depends on the instantaneous cluster temperature at which the monomers evaporate, which results in a thermal distribution of product translational energies. The obtention of two rotational distributions indicates that two rotational excitation mechanisms occur during the scattering event. The first mechanism is related to evaporation from a dense, strongly rotationally hindered vapor cushion that is produced during impact of the cluster with the surface. In fact, this mechanism is supported by the analysis of cluster and monomer density profiles, which demonstrate, the existence of the vapor cushion during the impact event, and that very cold monomers evaporate from this dense region of the cluster. The second mechanism is related to evaporation from the less dense outskirts of the cluster.

T9 – 15:00

DFT Study of the Formation of Benzene from Acetylene on Iron Clusters, Fe_n ($n=1-4$)

Steeve Chrétien and Dennis R. Salahub*

Département de chimie, Université de Montréal, C.P. 6128, Succursale Centre-Ville, Montréal (Québec), H3C 3J7, Canada

** Steacie Institute for Molecular Sciences (SIMS), National Research Council of Canada, 100 Sussex Drive, Ottawa (Ontario) K1A 0R6, Canada, and Centre de Recherche en Calcul Appliqué (CERCA), 5160 boul. Décarie, bureau 400, Montréal (Québec), H3X 2H9, Canada*

The formation of benzene from acetylene on Fe [1] and from ethylene on Fe_4 [2] has been observed experimentally in the gas phase. We have used Density Functional Theory to investigate these reactions. Reaction profiles for the formation of benzene from acetylene on iron clusters, Fe_n ; ($n=1-4$), will be presented. We will demonstrate that the occupancy of the molecular orbitals is very important for the correct description of the ground state of iron clusters. Our calculations ruled out the participation of vinylidene in the mechanism. The experimental observation, for the cyclodimerization of $Fe(C_2H_2)_2$, is explained on the basis of spin conservation principle. Error bars and other limitations of the present study will be discussed.

[1] D. Schroder, D. Sulze, J. Hrusak, D. K. Bohme and H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* 110, 145 (1995).

[2] P. Schnabel, M. P. Irion and K. G. Weil, *J. Chem. Phys.* 95, 9688 (1991).

T10 – 15:20

A Six-Dimensional Variational Calculation of the Bending Energy Levels of the HF Trimer and DF Trimer

Xiao-Gang Wang and Tucker Carrington Jr.

*Département de chimie, Université de Montréal,
C.P. 6128, succursale Centre-ville, Montréal (Québec)
H3C 3J7, Canada*

The bending energy levels of HF trimer and DF trimer were calculated variationally using a six-dimensional kinetic energy operator derived by constraining the stretch degrees of freedom to their equilibrium values. A basis of direct products of spherical harmonics is used to represent the wavefunction. As many as 17 million basis functions are used to converge the low-lying levels.

The symmetry adapted Lanczos method is used to calculate levels of all symmetries from one sequence of matrix-vector products. Two efficient ways of implementing the symmetry adapted Lanczos methods are presented. To determine the concerted hydrogen bond breaking tunneling splitting in HF trimer and DF trimer one needs to use the D_{3h} point group. By doing D_{3h} calculations we find that the splitting is negligible for the low-lying levels. If the tunneling is unfeasible the appropriate group is C_{3h} .

Our calculation using the most accurate SO-3+HF3BG potential developed by Quack, Stohner and Suhm indicates that two gas phase overtone bending bands of HF trimer should be reassigned, and that the noble gas matrix spectra of the bending fundamental bands are significantly shifted from their gas phase counterparts.

A recent new development is to use Lebedev grid to do potential quadrature in the spherical harmonic basis. Compared with the direct product Gauss-Legendre and Gauss-Chebyshev quadratures, use of Lebedev grid reduces the size of grids by a factor of 3 and therefore the memory cost is considerably reduced.

T11 – 15:40

Theoretical Investigation of Charge Transfer to Solvent in Photoexcited $\Gamma(\text{CH}_3\text{CN})_n$ Clusters

Qadir K. Timerghazin, Tao-Nhân Nguyen, and Gilles H. Peslherbe

Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University, 1455 de Maisonneuve Blvd. West, Montréal, Québec, Canada, H3G 1M8

Photoexcitation of the iodide-acetonitrile clusters $\Gamma(\text{CH}_3\text{CN})_n$ ($n=1-2$) leading to charge-transfer-to-solvent (CTTS) precursor states have been investigated computationally. The resulting vertical excitation energies are in good agreement with experimental results. The picture that emerges from the calculations of $\Gamma(\text{CH}_3\text{CN})$ is that, upon photoexcitation, an electron is transferred from one of the iodide p orbitals to the acetonitrile molecule(s), where it is stabilized by interactions with the acetonitrile dipole and the electrophilic hydrogen atoms of the methyl group. The concept of asymmetric solvation in $\Gamma(\text{CH}_3\text{CN})_2$ cluster [C.E.H. Dessent, C.G. Bailey, M.A. Johnson, J. Chem. Phys., **103**, 2006 (1995)] was revisited in light of *ab initio* calculations. In addition to the two “classical” linear structures – with a symmetrically and an asymmetrically solvated iodide – that were postulated previously, a nonlinear hydrogen-bonded isomer was also found. The calculated dissociation energies and vertical excitation energies for the linear symmetric and nonlinear hydrogen-bonded $\Gamma(\text{CH}_3\text{CN})_2$ isomers are in very good agreement with experimental data, while the linear asymmetric structure appears unlikely to be involved in experiments. The importance of hydrogen-bonding in halide-acetonitrile clusters manifests itself, not only in the fact that a third nonlinear hydrogen-bonded isomer exists, but also in slight distortions of the “classical” structures.

St. Hilaire, the Idea, the Place, the People and the Success

M.A.Whitehead

*Department of Chemistry, McGill University,
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Canada, H3A 2K6.*

The Educational and Intellectual Ideas which lead to the St. Hilaire Mini-Symposiums (1977-1978, 1980-1989, 1991-1995) will be related to the activities and demise of the series. The various Meetings surveyed for their Scientific and Personal interests, the attempts to run these Symposia at Queens (1979) and Ottawa (1990) will show the advantages of Symposia in Isolated place which trap the attendees in an environment which encourages free discussion and relaxed thinking. The problems of scientists unable to function without multi-media, and the mindless repetitive Centre of Excellence presentations will highlight the difference between knowledge and numerical results.

Posters

P1

Investigation of a Possible Mechanism for the Formation of a cyclotrisilene. Francis L.W. Esmonde-White, Jason A.C. Clyburne* and Heidi M. Muchall; *Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University, 1455 de Maisonneuve Blvd. West, Montréal, Québec, Canada, H3G 1M8*; * *Simon Fraser University, Burnaby, BC*

Recent experimental studies have shown cyclotrisilene formation by treatment of halogenated silanes with potassium graphite. Due to a spiropentasiladiene formed as a byproduct, a disilyne and disilavinylidene have been suggested as intermediates. This study is an investigation of the potential energy surface to elucidate the mechanism of formation of the cyclotrisilene, as well as to probe the nature of the disilyne.

P2

Theory within the Framework of Time-Dependent Density-Functional Theory: The "Loc.3" Approximation for the Calculation of NMR Shielding Parameters. Elisa Fadda, Mark E. Casida* and Dennis R. Salahub**.; *Département de chimie, Université de Montréal, C.P. 6128, Centre-ville, Montréal, H3C 3J7*; * *Laboratoire d'Etudes Dynamiques et Structurales de la Selectivite (LEDSS), Université Joseph Fourier (Grenoble I), France*; ** *The Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, ON-K1A 0R6*

Sum-Over-State Density-Functional Perturbation Theory (SOS-DFPT) [1] has been widely recognized as a significant step forward in the calculation of NMR parameters. One reason for this success is the ability to study larger molecules than with Hartree-Fock-based methods, as MP2 or CC. At its conception, neither ideas from relativistic nor from current density-functional theory were used in the development of SOS-DFPT. Instead a pragmatic approach was taken and observed errors in excitation energies were corrected via ad hoc approximations known as local approximation 1 ("Loc.1") and local approximation 2 ("Loc.2"). The present work [2] shows how these approximations can be derived from Time-Dependent Density-Functional Theory (TDDFT) without either relativistic or current-density functionals. In particular, we will show how the introduction of the Tamm-Dancoff Approximation (TDA) puts magnetic and electric perturbations on the same footing. At that point the connection between SOS-DFPT and TDDFT is easily found through the Two-Level approximation (2L) that introduces what we named the "Loc.3" approximation, in analogy with "Loc.1" and "Loc.2". We will show and analyse the results of numerous tests of the "Loc.3" approximation against the SOS-DFPT local and uncoupled (UKS) approximations and against some of the most recent and most promising functionals for the calculation of NMR shielding parameters. The analysis the results has lead us to the conclusion that, not only does the "Loc.3" approximation represent a rigorous physical basis for SOS-DFPT, but our work also opens the way to a further improvement of the DFT-based NMR parameter calculation.

References: [1] V. G. Malkin, O. L. Malkina, M. E. Casida, and D. R. Salahub, *J. Am. Chem. Soc.* **94**, 5898 (1994); [2] E. Fadda, M. E. Casida, and D. R. Salahub, *Int. J. Quant. Chem.* submitted.

P3

Molecular Modelling of Poly(Ethylene Oxide) Model Cofactors; 1,3,6-tri-o-galloyl- β -D-glucose and Corilagin. Roger Gaudreault, Theo G. M. van de Ven, Michael A. Whitehead; *Department of Chemistry, McGill University, 801, Sherbrooke Street West, Montreal, Quebec, Canada, H3A 2K6.*

The most stable structures of two poly(ethylene oxide) (PEO) model cofactors, β -1-O-Galloyl-3,6-(R)-hexahydroxydiphenoyl-D-Glucose (corilagin) and 1,3,6-Tri-O-Galloyl- β -D-Glucose (TGG), are calculated using Molecular Modelling and PM3 Semi-Empirical Molecular Orbital Theories. The theoretical PM3 structures agree with interpreted structures from experimental NMR; the glucopyranose ring of corilagin has a boat and TGG a chair conformation, for which the heats of formation, torsion angles, distances, van der Waals surface, and the infrared spectra are calculated.

P4

Does Guanidine Hydrochloride Interact with a Polypeptide Backbone ? Hasnain Gulam, Gilles H. Peslherbe and Ann M. English; *Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University, 1455 de Maisonneuve Blvd. West, Montréal, Québec, Canada, H3G 1M8*

Protein folding problem has received much attention recently. How protein folds into its three dimensional and functional structure given its primary sequence of amino acids is quite intriguing. For practical reasons, researchers often study protein unfolding to investigate types of interaction that hold the protein in its native structure. Chemical denaturants such as guanidine hydrochloride (GdnHCl) is widely used to denature proteins. However, not much is known about their interaction with proteins especially at the atomic level. Does GdnHCl interact with backbone of a polypeptide and disrupt the bonding involved? We make use of FT-IR spectroscopy to gain insight, at atomic level, on the type of interaction involved between GdnHCl and a homopolypeptide, poly-L-lysine (PLL). In addition, molecular modeling is employed to confirm the nature of this interaction. A surprising result suggests that GdnHCl interacts with the lysine side chain of PLL and the backbone of the polypeptide remains unaffected.

P5

On the Nature of Bonding Interactions in Small Metal Ion-Water Clusters. Sean R. Hughes, John A. Capobianco and Gilles H. Peslherbe; *Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University, 1455 de Maisonneuve Blvd. West, Montréal, Québec, Canada, H3G 1M8*

The study of aqueous clusters containing metal ions has garnered much attention over the years. However, the nature of the bonds between metal ions and water ligands are still questionable. This interaction has been reported to be strongly covalent in some complexes (eg. $[\text{Be}(\text{H}_2\text{O})_2]^{2+}$) and ionic in others (eg. $[\text{Na}(\text{H}_2\text{O})_2]^+$). In addition, heavy metal dihydrates appear to prefer a C_2 or C_2 'bent' structure as opposed to a D_{2d} linear arrangement. Recent advances in theoretical chemistry, such as Bader's *Atoms in Molecules* (AIM) or Becke and Edgecombe's *Electron Localization Function* (ELF), may provide qualitative and quantitative insight into the nature of bonding in molecules. We have chosen to employ these methods to explore how water binds to metal ions in small clusters (dimers and trimers) and to determine the forces that govern this interaction. A combination of ELF and AIM analyses, as well as *ab initio* calculations of the energetic, structural and electronic properties were employed. We find that all metal-water interactions studied show distinct ionic character and that induction effects play a pivotal role in the geometric arrangements of these structures.

P6

Thermodynamics of Surface vs. Interior Solvation in Halide-Water Clusters. Denise M. Koch and Gilles H. Peslherbe; *Centre for Research in Molecular Modeling and Departement of Chemistry & Biochemistry, Concordia University, 1455, de Maisonneuve blvd West, Montreal, Quebec, Canada H3G 1M8*

A quantitative investigation of surface vs. interior solvation in halide-water clusters was performed by evaluating the potentials of mean force and structural properties of $X^-(\text{H}_2\text{O})_n$ clusters ($X=\text{F,Cl,Br,I}$ and $n=32,64$) from Monte Carlo simulations with both non-polarizable and polarizable model potentials. Simulation results clearly indicate that the chloride, bromide and iodide ions tend to reside at the surface of water clusters of sizes between 12 and 32, whereas entropy and polarization effects make the interior solvation state more likely for cluster sizes between 20 and 64, depending on the size and the polarizability of the halide ions. This is consistent with previous analyses of cluster experimental and model data, which suggest a gradual transition from surface to bulk behavior for large halide ions.

P7

Rationale for reagent reorientation in a triatomic bimolecular collision: The linear Transformation model. P. Larrégaray, L. Bonnet* and J.-C. Rayez,* *Departement of Chemistry and Biochemistry, Concordia University, 1455, de Maisonneuve blvd West Montreal, Quebec, CANADA H3G 1M8, * Laboratoire de Physico-chimie Moléculaire 351, cours de la libération, 33405 Talence Cedex*

The reaction $\text{N}(\text{C}^2\text{D}) + \text{H}_2(\text{X}^{1/2}\text{e}^+)? \text{NH}(\text{X}^{3/2}) + \text{H}(\text{S})$ involves an early barrier of ~ 2 kcal/mol and a significant exoergicity of ~ 30 kcal/mol. Thus, for collision energies of several kcal/mol, barrier crossing leads to reaction with nearly unit probability. To our knowledge, the angular dependent line of center (ADLOC) model is to date the only one which allows the analytical formulation of the barrier overcoming cross section, identifiable here with the reaction cross section. This model, however, neglects the interaction between reagents up to the barrier top. As a consequence, it ignores the strong reorientation of H_2 with respect to N which enhances, on the average, the reactivity with respect to its predictions. The linear transformation model¹ (LTM), recently derived in order to describe product separation in unimolecular fragmentations, is now applied to the study of reagent approach in the title reaction. The main interest of LTM is to take into account reorientation while leading to an expression of the reaction cross section as simple as the ADLOC one, but in better agreement with dynamical calculations.

¹ P.Larregaray, L. Bonnet and J.-C. Rayez, *J. Chem. Phys.* 114, 9380 (2001)

P8

A Theoretical Investigation of 1,2-Migrations in Methoxysiloxycarbene. P.G. Loncke and Gilles H. Peslherbe; *Centre for Research in Molecular Modeling and Departement of Chemistry & Biochemistry, Concordia University, 1455, de Maisonneuve blvd West, Montreal, Quebec, Canada H3G 1M8*

Intramolecular rearrangements of methoxysiloxycarbene ($\text{H}_3\text{COCOSiH}_3$) have been investigated by means of *ab initio* molecular orbital theory and hybrid density-functional theory calculations. Particular attention has been paid to 1,2-silyl migration from oxygen to the carbene carbon, and to the analog 1,2-methyl migration for comparison. A combination of frontier molecular orbital (FMO) theory, natural bond orbital (NBO) analysis, the theory of atoms in molecules (AIM) and the electron localization function (ELF) were used to shed light onto the mechanistic details of these rearrangements. The present analyses clearly indicate that 1,2-silyl migration involves nucleophilic attack by the carbene lone pair at silicon, while 1,2-methyl migration seems to involve an anion-like shift of the methyl group from oxygen to the "vacant" carbene p orbital. Finally, computed relative Gibbs free energies suggest that 1,2-silyl migration is much more favorable than 1,2-methyl migration in accord with experimental findings.

P9

Conformation and Interactions of poly(styrene maleic anhydride) chains in water. Cecile Malardier-Jugroot, Theo G. M. van de Ven, Michael A. Whitehead; *Department of Chemistry, McGill University, 801, Sherbrooke Street West, Montreal, Quebec, Canada, H3A 2K6.*

Surface sizing is an important part of the paper making process; it prevents water from penetrating the paper and therefore enhances printing. The sizing agent studied in this project is the poly(styrene maleic anhydride) (SMA). Experimental studies have determined that SMA chains associate with themselves to form macro-coils at neutral pH but no association has been observed at low or high pH. This association has been proposed to be a zipping process between the chains at the air/water interface and in the water.

A conformational study of SMA at different pH(3,7,12) has already performed using the semi-empirical PM3 theory. Two methods were used to determine the conformation of SMA: the energy-optimised tree branch method and series of scans in energy around the dihedral angles of the polymer for the three degrees of ionisation of the monomer. The structures obtained have been reoptimised at the *ab initio* RHF/6-31G level.

The study of polymers in solvents is very challenging and implicit and explicit solvent models have been recently developed. The hydrogen bonds between the hydrophilic part of SMA and the water molecules are not described in the implicit models, therefore an explicit model is essential to reproduce the first and second shells of solvation and to model the interactions of SMA with water at different pH (3,7,12). This explicit solvent model will use the semi-empirical PM3 to model the hydrophobic interactions between the styrene groups of SMA and the solvent and *ab initio* RHF method to reproduce the hydrophilic interactions between the carboxyl groups and the solvent. An average effect of all other shells of solvation will be reproduced using either a continuum model or an explicit solvent model treated by molecular mechanics.

P10

Computational Studies of N-Phenyl-N'-Sulfinylhydrazines. Pratibha Malla and Heidi M. Muchall; *Centre for Research in Molecular Modeling and Departement of Chemistry & Biochemistry Concordia University, 1455, de Maisonneuve blvd West, Montreal, Quebec, Canada H3G 1M8*

Ab initio quantum chemical and density functional theory (DFT) methods are used in order to investigate the geometries of substituted N-phenyl-N'-sulfinylhydrazines, Ar-NH-N=S=O. The computational results reveal that in all cases the syn configuration is the most stable, whereas anti and sickle configurations are higher energy minima. Frequency calculations are performed on the optimized structures in order to aid the interpretation of experimental IR studies.

P11

Quantum Mechanical Approaches for Paramagnetic NMR Shifts in Density Functional Theory. Seongho Moon, Serguei Patchkovskii, Dennis R. Salahub; *Département de chimie, Université de Montreal, Département de chimie, Université de Montréal, C.P. 6128, succursale Centre-ville, Montréal (Québec) H3C 3J7, Canada; National Research Council Canada, Ottawa, Ontario, Canada K1A 0R6*

The paramagnetic NMR contributions are investigated by the analysis of the quantum mechanical magnetic energy levels using the effective spin Hamiltonian.

In this study, the zero field splitting and the second order Zeeman mixing are neglected. The field from the magnetic moment of the electron is averaged to account for the fast relaxation between the two electronic states. The paramagnetic shift terms are described by the product of the hyperfine coupling tensor and the electronic g-tensor. The shifts are calculated in density functional theory and the simple application to a biological system is discussed.

P12

Molecular Vibrational excitation in Surface-Induced Fragmentation of $(\text{N}_2)_n$ and $(\text{O}_2)_n$ clusters. Tao-Nhan Nguyen, Holger Vach* and Gilles H. Peslherbe; *Centre for Research in Molecular Modeling and Departement of Chemistry & Biochemistry, Concordia University, 1455, de Maisonneuve Blvd West, Montreal, Quebec, Canada H3G 1M8*; * *Centre for Research in Molecular Modeling, Concordia University, and Laboratoire de Physique des Interfaces et des Couches Minces C.N.R.S. - Ecole Polytechnique, 91128 Palaiseau, France*

This study was motivated by the promising and unexplained oxidation processes when using a $(\text{O}_2)_m$ cluster beam on silicon surfaces¹. The tentative explanation that was brought invokes a cluster-catalyzed oxidation via a molecular oxygen dissociation channel, akin to processes observed in the famous "burning of air"². In the molecular dynamics simulations presented in this work, we carried on a comparative study between $(\text{N}_2)_m$ and $(\text{O}_2)_m$ clusters impacted on two surface reflexion models, using classical potentials and semiempirical methods. We showed that, when impacting larger cluster on silicon surfaces, the cluster does not catalyze monomer vibrational excitation, since the vibrational energy actually gets distributed over the monomers. The vibrational energy distribution reproduced a single Boltzmann-type distribution, with monomers found in the ground or first excited quantum vibrational states. When varying the incident cluster velocity, we observed that a very large incident kinetic energy was necessary to obtain significant probability of dissociation, i.e. about 5 times the experimental value. When using a different surface model including surface-to-cluster heat transfer effect showed that this factor was also not sufficient either to allow for O_2 dissociation at experimental conditions.

¹ D.V. Daineka, F. Pradere, M. Chatelet, E. Fort, manuscript in preparation.

² T. Raz, R.D. Levine, Chem. Phys. Lett., **246**, 405, (1995).

P13

Improving "Difficult" Reaction Barriers with Self-Interaction Corrected DFT. Serguei Patchkovskij and Tom Ziegler;* *Steele Institute for Molecular Sciences, Ottawa, Ontario, K1A 0R6, Canada*; **Department of Chemistry, University of Calgary, 2500 University Dr. NW, Calgary, Alberta, T2N 1N4 Canada*

We examined eleven "difficult" reactions with self-interaction corrected density functional theory. The data set includes dissociation of radicals into symmetric fragments ($\text{H}_2 \rightarrow \text{H} + \text{H}^\cdot$, $\text{He}^{2+} \rightarrow \text{He} + \text{He}^\cdot$), radical hydrogen abstraction ($\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}^\cdot$, $\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}^\cdot$, $\text{H} + \text{N}_2\text{H}_2 \rightarrow \text{N}_2\text{H} + \text{H}_2$, $\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}^\cdot$), proton transfer ($\text{HC}(\text{OH})\text{CHC}(\text{O})\text{H} \rightarrow \text{HC}(\text{O})\text{CHC}(\text{OH})\text{H}$), $\text{S}_\text{N}2$ halogen exchange ($\text{X}^\cdot + \text{CH}_3\text{X} \rightarrow \text{CH}_3\text{X}^\cdot + \text{X}$, $\text{X}=\text{F}, \text{Cl}, \text{Br}$), and closed-shell unimolecular dissociation of tetrasine ($\text{C}_2\text{N}_4\text{H}_2 \rightarrow \text{N}_2 + 2 \text{HCN}$). Calculated self-interaction energies cancel, almost identically, for the reaction energies (dE_r), so that SIC functionals do not lead to a systematic improvement in dE_r . Self-interaction correction increases for reaction transition structures, leading to higher calculated activation barriers (dE^\ddagger). The average absolute deviation in dE^\ddagger from ab initio and experimental barriers, is reduced from 14 (VWN) or 12 (revPBE) kcal/mol to 5.4 (SIC-VWN) or 3.4 (SIC-revPBE) kcal/mol. Gradient-corrected functionals (revPBE, BP86) reduce the magnitude of the total self-interaction correction, by improving the description of the core orbitals. For the valence orbitals, both the magnitudes of the self-interaction corrections, and their change between reagents and transition structures, are similar for VWN LDA, and GGA functionals. Reducing the magnitude of the self-interaction energy for valence electrons thus appears to be a promising direction for the development of chemically accurate exchange correlation functionals.

P14

On the Regioselectivity of Nitrilimine Cycloadditions. Cyril Puel and Gilles H. Peslherbe; *Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University, 1455 Blvd de Maisonneuve west, Montréal (Québec), Canada H3G 1M8.*

A combination of quantum chemistry and Frontier Molecular Orbital theory is used to investigate the regioselectivity of nitrilimine cycloadditions with alkenes. Results previously reported and low-level theoretical studies seem to show some discrepancies regarding the dependence. We use FMO theory to predict the regioselectivity for a list of reactants and compare the results to experiments. Then four different substituted nitrilimines are studied in order to infer their cycloaddition reaction mechanism and determine whether substituents play a major role in the regioselectivity of the reaction. Those nitrilimines will be then compared to the unsubstituted to evaluate the substituent influence. The electronic structure of the nitrilimine is also discussed.

P15

A Theoretical and Experimental Study of Photoswitching Hydrogen-bonded Azodibenzoic Acids. F. Rakotondradany, M.A. Whitehead and H. Sleiman*; *Department of Chemistry, McGill University, 801, Sherbrooke Street West, Montreal, Quebec, Canada, H3A 2K6.*

Hydrogen bonds have been used extensively to build molecular tapes and hexameric rosettes (1). Experimental and theoretical understanding of those self-assembled supramolecules is an expanding area of research. Photochromic *trans* azobenzene is incorporated in the backbone of such weakly bound oligomers. The theoretical study of the hydrogen-bonding gives a better insight into the molecular organization. The most stable isomer, (*trans*) azodibenzoic acid should form linear tapes. The *cis* photoisomer can yield all-*cis* tapes but also square or hexameric rosettes inducing photoamplification.

Full energetics and vibrational analyses of the geometry optimized 1- to 6-mers are done using the semi-empirical PM3 theory in terms of enthalpy and entropy of formation. PM3 energy optimizations of several oligomer conformations are carried out to find the most thermodynamically stable supramolecule from either the *trans* or the *cis* isomer (2). All PM3 semi-empirical results suggest that *trans* isomers form tapes and *cis* isomers rosettes. A comparison between the most stable *cis* aggregates, square and cyclic hexamer is made in terms of energetics and geometry to predict the shape and size of the discrete supramolecule.

The PM3 optimization of the hydrogen-bonded isophthalic acid aggregates, which are well-known experimentally (3), is also carried out to fully validate the PM3 predictions.

(1) I. S. Choi, X. Li, E. E. Simanek, R. Akaba, and G. M. Whitesides, *Chem. Mater.* 1999, 11, 684 and references therein.

(2) F. Rakotondradany, M.A. Whitehead, and H. Sleiman, Photoswitching hydrogen-bonded azodibenzoic acids: theory and synthesis.

(3) J. Yang, J.L. Marendaz, S. J. Geib, and A. D. Hamilton, *Tet. Lett.*, 1994, 35, 22, 3665.

P16

A Theoretical Study of the Atmospheric Reaction of Carbonyl Oxide with Water Vapor. Andrew Ryzhkov, Parisa Ariya, Henry Leighton; *Departments of Chemistry and Atmospheric & Oceanic Sciences, McGill University, 801 Sherbrooke St. W., Montreal, Quebec, Canada, H3A 2K6*

Theoretical investigations of the atmospherically important gas-phase reaction mechanism of the parent and methyl-substituted carbonyl oxide with water reaction were carried out. The B3LYP method with the 6-31G(d,p) and 6-311+G(2d,2p) basis sets was used for the geometry optimizations of the stationary points and the transition states search. Additionally, single-point CCSD(T)/6-311+G(2d,2p) energy calculations were performed for the B3LYP/6-311+G(2d,2p) structures. First, the reaction begins with the formation of a hydrogen-bond complex between reactants. Then, we supposed three different channels of the reaction leads to formations of the molecular products. The first one is formation of hydroxymethyl hydroperoxide (HMHP) in case simple carbonyl oxide and accordingly 1-hydroxyethyl hydroperoxide (1-HEHP) in case methyl-substituted one. The second one gives carbonyl compound and hydrogen peroxide. The third way leads to formation of hydrotrioxide. We have found that the energetically most favorable pathway of the reaction is formation the hydroxyalkyl hydroperoxide.

P17

Structures and Stability of CO and N₂ Physisorbed on MgO: Descending the Devil's Staircase. A. K. Sallabi and D. B. Jack; *Centre for Research in Molecular Modeling and Department. of Physics and Department. of Chemistry & Biochemistry, Concordia University, 1455, de Maisonneuve blvd West, Montreal, Quebec, Canada H3G 1M8*

Metropolis Monte Carlo simulations are performed to study the structures and stability of CO and N₂ molecules physisorbed on the MgO(001) surface. Below 41 K the CO molecules form a c(4x2) structure which consists of alternating rows of densely packed tilted molecules separated by rows of less dense perpendicular molecules. Above 41 K, and at low pressures, this phase undergoes a phase transition to a less dense disordered phase via the expulsion of molecules. A further transformation to a p(3x2) phase is possible by converting tilted to perpendicular molecules. A model to test the relative stability of the c(4x2) and p(3x2) phases shows that at sufficiently high pressures and temperatures the p(3x2) phase is more stable than the c(4x2) phase as found experimentally. We propose that a sequence of transitions through a set of (nx2)-type structures with ever decreasing density is possible under suitable conditions of temperature and pressure. This sequence of transitions is an example of devil's staircase phenomenon as has been suggested by LEED experiments. A similar devil's staircase sequence is found for N₂/MgO(001) system. These structures are in agreement with neutron and helium atom scattering results.

P18

Theoretical Evidence for the Catalytic Role of Metal Copper Ions in the Degradation of S-nitrosothiols. Céline Toubin, David Y.-H. Yeung, Ann M. English and Gilles H. Peslherbe; *Centre for Research in Molecular Modeling and Department. of Chemistry & Biochemistry, Concordia University, 1455, de Maisonneuve blvd West, Montreal, Quebec, Canada H3G 1M8*

S-Nitrosothiols are known to be an important source of NO, which plays a key role in blood pressure regulation. RSNOs are easily formed in vivo by nitrosation of RSH species. The degradation of RSNOs leading to NO release, is believed to be catalyzed by copper ions (Cu^I) which are continuously regenerated in vivo. Kinetic experiments showed that decomposition rates upon Cu^I catalysis vary significantly with the chemical nature of the RSNO considered. The reaction mechanism remains still unclear.

In this paper, on the basis of first-principles calculations, the catalytic role of copper ions Cu^I is investigated for S-Nitrosocysteine, which was shown to be rapidly degraded by Cu^I , and for comparison, for other S-Nitrosocysteine derivatives.

P19

Spin-current Modulation and Square-wave Transmission Through Periodically Stubbed Electron Waveguides. X. F. Wang, P. Vasilopoulos, and F. M. Peeters;* *Department of Physics, Concordia University, 1455 de Maisonneuve West, Montreal, Quebec, H3G 1M8, Canada; * Departement Natuurkunde, Univrsiteit Antwerpen (UIA) Universiteitsplein 1, B-2610, Belgium.*

Ballistic spin transport through waveguides, with symmetric or asymmetric double stubs attached to them periodically, is studied systematically in the presence of a weak spin-orbit coupling that makes the electrons precess. 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-type behavior, with values 1 and 0, with wide gaps when only one mode is allowed to propagate in the waveguide. A similar behavior is possible for a certain range of the stub parameters even when two-modes can propagate in the waveguide and the conductance is doubled. Such a structure is a good candidate for establishing a realistic spin transistor. A further modulation of the spin current can be achieved by inserting defects in a finite-number stub superlattice. Finite-temperature effects on the spin conductance are also considered.

P20

Mass Spectrometric Protein-based Radical Spin Probing. John Wright and Ann M. English; *Centre for Research in Molecular Modeling and Department. of Chemistry & Biochemistry, Concordia University, 1455, de Maisonneuve blvd West, Montreal, Quebec, Canada H3G 1M8*

Heme peroxidases play many roles in vivo including hormone synthesis signal transduction and cellular protection. Their reaction occurs through a two-step mechanism where a peroxide reacts with the ferric heme and the two oxidizing equivalents of the peroxide are retained by the enzyme as a $\text{FeIV}=\text{O}$ species and a porphyrin or polypeptide-based radical cation. Cytochrome c-peroxidase (CCP) in the absence of donor substrate can reduce up to 10 equivalents of H_2O_2 by forming multiple polypeptide-based radicals. These oxidizing equivalents may be involved in signal transduction radical translocation substrate oxidation or oxidative damage. The detection and characterization of protein-based radicals has been difficult due to their high reactivity and low concentration. Recently we have described a new tool for the unambiguous identification of protein-based radicals. To date protein-radical detection by electrospray mass spectrometry (ESI-MS) has been modeled after electron paramagnetic resonance (EPR) experiments where diamagnetic spin traps react with protein radicals to form more stable spin adducts. Since a mass change and not an unpaired spin is necessary for MS detection stable paramagnetic molecules such as 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) can be used for the identification of protein-based radicals. The horseradish peroxidase (HRP/ H_2O_2) reaction was used as a model for radical generation in biological systems and derivatives of phenylalanine tryptophan and tyrosine were incubated in a mixture of HRP/ H_2O_2 and TEMPO and the products analyzed by electrospray MS. A 50-fold increase in sensitivity as obtained using TEMPO as a radical scavenger compared to previous MS-based methods using spin-traps. The electrospray mass spectra of TEMPO and several derivatives exhibit molecular ions arising from oxidation rather than protonation which is somewhat unusual in ESI. MS/MS is being used to further characterize the fragmentation pattern of the TEMPO derivatives. Another interesting observation in the mass spectrum is a peak corresponding to a proton-bridged TEMPO dimer. This dimer has been modeled using ab initio calculations. The goal of this work is to characterize protein-based radicals formed in CCP HRP and myoglobin in high H_2O_2 environments using the ESI-MS/MS spin-probing protocol. The modified enzymes will be digested and the residues labeled with TEMPO determined by peptide mass mapping and sequencing by MS/MS. Understanding the mechanism of radical translocation by heme peroxidases will aid in the development of more stable heme peroxidases for industrial purposes and shed light on the mechanism of heme-enzyme mediated oxidative stress and redox H_2O_2 signalling in vivo.

Structural Determination of Calbindin-D_{28K} using Intramolecular Cross-linkers, Mass Spectrometry and Molecular Mechanics. David Yong-Hoi Yeung, Ann M. English and Gilles H. Peslherbe; *Centre for Research in Molecular Modeling and Department of Chemistry & Biochemistry, Concordia University, 1455, de Maisonneuve Blvd West, Montreal, Quebec, Canada H3G 1M8*

Conventional methods for structural determination of proteins include NMR and X-ray crystallography. However, these methods have limitations. Recently, a study by Young *et. al.* suggested the possibility of tertiary structural characterization of proteins with the use of sequence alignment, chemical cross-linkers and mass spectrometry. Our research interest lies in the characterization of the tertiary structure of a calcium binding protein, human calbindin-D_{28K} using the approach mentioned above. In addition, the proposed structure obtained from these experiments will be modeled using molecular mechanics. The simulations will aid in the design of the experiments, allow us to refine the structure, and suggest other conformations that the protein may adopt, either in its apo or holo form.

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