

5th CERMM Annual Symposium

**Program and
Book of Abstracts**

February 11-13, 2005

**Richard J. Renaud Science Complex,
Concordia University**

CERMM Director's Foreword

Computational and theoretical chemistry has been widely recognized as a growing and indispensable branch of science in the past decade. This claim is supported by the awarding of the 1998 Nobel Prize in Chemistry to quantum chemists Walter Kohn and the late John Pople (who sadly passed away last year), the launching of two new journals, the *Journal of Theoretical and Computational Chemistry* (World Scientific) in 2002 and the *Journal of Chemical Theory and Computation* (American Chemical Society) in 2005, and the appointment at many Canadian institutions of Canada Research Chairs and University Research Chairs in computational chemistry and biochemistry. Advances in computer hardware and software are propelling the rise of computational and theoretical chemistry as a dynamical field that makes the cover of international scientific magazines such as *Chemical & Engineering News* and *Physics Today* on a regular basis.

Traditionally, computational and theoretical chemistry has been a scientific force in Canada, particularly in the Montreal area. Our Faculty of Arts and Science here at Concordia University recognized this fact over 5 years ago. Envisioning the growing importance of computational and theoretical chemistry in modern research, the Faculty supported and encouraged the establishment of the Centre for Research in Molecular Modeling (CERMM) in 2000. The mission of CERMM is to promote excellence in research and graduate education in computational chemistry and biochemistry, to foster collaborations between researchers in different institutions, and to provide an interdisciplinary forum for experimentalists, modelers and theoreticians to combine their expertise to reach new frontiers in the molecular sciences.

CERMM has grown into a multi-institutional centre with 14 senior members from 6 institutions with diverse interests. The infrastructure available in CERMM currently supports the research of over 10 postdoctoral fellows, 35 graduate students and numerous undergraduate students in atmospheric, biological, inorganic, macromolecular, materials, medicinal, organic, physical, and polymer chemistry. All interested researchers in the molecular sciences are more than welcome to become new members of CERMM.

The annual CERMM symposium provides a unique opportunity for us to showcase the research carried out here in the Centre and at participating institutions. More importantly, it allows all researchers in the field of molecular modeling (as broadly defined) to present and discuss their work, to share new knowledge, and to envisage new collaborations. Such activities are critical in promoting science and higher education in our field.

The symposium would not happen without the invaluable help of CERMM students and postdoctoral fellows in the logistics of symposium organization. I would like to thank, in particular, Grygoriy Dolgonos, Elena Ivanova, Denise Koch, Robert Mawhinney, Qadir Timerghazin and Sacha Zlatkova for the great work they have done.

Enjoy the symposium!



Gilles H. Peslherbe, CERMM Director

Symposium Program

Friday, February 11, PM, Room SP-S-110

4:30 Registration

Chair: Gilles Peslherbe (Concordia University)

5:00 Opening address

Dr. June Chaikelson (Dean of Arts and Science, Concordia University)

5:15 Plenary lecture and Merck-Frosst Lecture

Emily A. Carter (Professor of Mechanical & Aerospace Engineering, and Chemistry & Chemical Engineering, Princeton)

Stressed-Out Metals: Predicting Their Response from the Bottom Up

6:15 Wine and Cheese Reception

Saturday, February 12, AM, Room SP-S-110

8:30 Registration

Chair: Matthias Ernzerhof (Université de Montréal)

9:00 Marcel Nooijen (University of Waterloo)

State-Selective Internally-Contracted Multireference CC Approach vs. Single Reference CCSD + Extensive Renormalized Triples Corrections

9:40 Radu Iftimie (Université de Montréal) and Mark Tuckerman (New York University)

Car-Parrinello Molecular Dynamics: An Application to the Decomposition of IR Spectra of Aqueous Systems into Solute and Solvent Contributions

10:00 Andriy Plugatyr and Igor M. Svishchev (Trent University)

Hydroxyl Radical and Phenol in Aqueous Solution: Computer Simulation

10:20 Coffee break

Chair: Heidi Muchall (Concordia University)

10:40 Viktor N. Staroverov, Gustavo E. Scuseria (Rice University), John P. Perdew, Jianmin Tao (Tulane University, New Orleans), and Ernest R. Davidson (University of Washington)

Highly Charged Ions: A Challenge for Density Functional Theory

11:00 Robert C. Mawhinney, Heidi M. Muchall and Gilles H. Peslherbe (Concordia University)

Revisiting the 1,3-Dipolar Cycloaddition Mechanism: Nitrilimines as a Case Study

- 11:20** Elena V. Ivanova and Heidi M. Muchall (Concordia University)
Theoretical Study of the Hydrolysis of N-Sulfinylamines
- 11:40** Andrew Ryzhkov and Parisa Ariya (McGill University)
A Theoretical Study of Criegee Intermediate Complexes with Water Clusters and its Reactions in the Atmosphere
- 12:00** Michael Lever (Canterbury Health Centre, New Zealand), Robert G.A.R. Maclagan (University of Canterbury, Christchurch, New Zealand), Cecile Malardier-Jugroot and M.A.Whitehead, (McGill University)
An Explanation of the Denaturing of Proteins

12:20 Lunch, poster session and vendor exhibition, SP-S Atrium

Saturday, February 12, PM, Room SP-S-110

Chair: Robert LeRoy (University of Waterloo)

- 3:00** Tucker Carrington (Université de Montréal)
New Tools for Studying the Dynamics of Small Molecules: Ideas and Applications
- 3:40** Xiaogang Wang, Tucker Carrington Jr., J. Tang, and A.R.W. McKellar (Université de Montréal)
Quantum Calculation of Rovibrational Spectra of OCS-He₂, N₂O-He₂ and CO₂-He₂
- 4:00** Richard Dawes, Tucker Carrington Jr. (Université de Montréal)
How to Choose 1-D Basis Functions so that a Very Efficient Multidimensional Basis may be Extracted from a Direct Product of the 1-D Functions: Energy Levels of Strongly Coupled Systems with as many as 16 Coordinates

4:20 Coffee break

Chair: David Wardlaw (Queen's University)

- 4:40** Bilkiss Issack and Pierre-Nicholas Roy (University of Alberta)
Constrained Semiclassical Molecular Dynamics
- 5:00** Afshin Eskandari Nasrabad, Rozita Laghaei, and Byung Chan Eu (McGill University)
Molecular Theory of Transport Properties of Liquid Carbon Dioxide
- 5:20** Tao Peng and Robert J. Le Roy (University of Waterloo)
IR Shifts of SF₆ in an Ar Matrix and Fitting Spectra Utilizing a Genetic Algorithm
- 5:40** Denise M. Koch and Gilles H. Peslherbe (Concordia University)
Thermodynamics of Surface vs. Interior Solvation in Halide-Water Clusters
- 6:00** Qadir K. Timerghazin and Gilles H. Peslherbe (Concordia University)
Potential Energy Surfaces and Dynamics of the Charge-Transfer-To-Solvent (CTTS) Excited and Ionized States of Iodide-Acetonitrile Clusters

6:30 Symposium Banquet

Sunday, February 13, AM, Room SP-S-110

Chair: Régis Pomès (University of Toronto)

9:00 François Major (Université de Montréal)

Using Nitrogen Base Cyclic Motifs as RNA Building Blocks

9:40 Qishi Du, (Tianjin Institute of Bioinformatics and Drug Discovery and Tianjin Normal University, China), S. Sirois, (Université du Québec à Montréal), Kuo-Chen Chou, (Tianjin Institute of Bioinformatics and Drug Discovery and Tianjin Normal University, China and Gordon Life Science Institute, San Diego), Dongqing Wei (Tianjin Institute for Bioinformatics and Drug Discovery and Concordia University)

Bioinformatics and Its Application on Inhibitor Design Against SARS

10:00 Christopher Baker (Concordia University) and Rene Witte (Universität Karlsruhe)

Mutation Miner - Textual Annotation of Protein Structures

10:20 Etienne Paradis, Ann M. English and Gilles H. Peslherbe (Concordia University)

Ca²⁺ Binding to Calbindin D28K: A Molecular Dynamics Study

10:40 Coffee break

Chair: Ann English (Concordia University)

11:00 James Gauld (University of Windsor)

Computational Investigations on Biochemical Catalysis

11:40 Rami Hourani, Ashok Kakkar, and M. A. Whitehead (McGill University)

3,5-Dihydroxybenzylalcohol Based Dendrimers: Structure Evaluation and Molecular Encapsulation in Generations 1-5

12:00 Suzanne Sirois (Université du Québec à Montréal), E. I. Proynov (Edmonston University), J. F. Truchon (Merck Frosst), C. M. Tsoukas (McGill University), D. R. Salahub (University of Calgary)

A Density Functional Study of the Hydrogen-Bond Network Within the HIV-1 Protease Catalytic Site Cleft

12:20 Régis Pomès, Tomas Rodinger, and Chris Madill (Hospital for Sick Children and University of Toronto)

Probing Hydrophobic Association and Protein-Ligand Binding with Free Energy Simulations in Four Spatial Dimensions

12:40 Petrina Kamyra and Heidi M. Muchall (Concordia University)

A Quantum Chemical Analysis into the Stabilizing Interactions in Nucleic Acid Base Pairs

13:00 Closing

POSTER PRESENTATIONS

Saturday, February 12, 12:30 – 3:00 PM
SP-S Atrium

- 12:30 - 1:45 Those whose papers were given (A) labels (1A, 2A, 3A, etc.) should attend their posters.
- 1:45 - 3:00 Those whose papers were given (B) labels (1B, 2B, 3B, etc.) should attend their posters.

- 1A Ivan Vinogradov, Darren Anderson, and M. Cynthia Goh (University of Toronto)
Molecular Simulations Performed with Collagen Monomer Model
- 1B K. R. Shamasundar and M. Nooijen (University of Waterloo)
Internally Contracted State-Selective Multi-Reference Methods Based on Equation-of-Motion Coupled-Cluster Approach
- 2A Qadir K. Timerghazin, Tao-Nhân V. Nguyen, and Gilles H. Peslherbe (Concordia University)
Halide Ions in a "Methyl Pocket": Competition between Hydrogen Bonding and Ion-Dipole Interactions
- 2B Svetlana Popenova, Philippe G. Merle, and Gilles H. Peslherbe (Concordia University)
Computational Studies of Agostic Interactions between Substituents on the Cyclopentadienyl Ring and the Metal in Zirconocenium Complexes
- 3A Grygoriy A. Dolgonos and Gilles H. Peslherbe (Concordia University)
A Computational Study of the Unimolecular C₂ Fragmentation of the C₈₂ Fullerene
- 3B Robert C. Mawhinney, Heidi M. Muchall, and Gilles H. Peslherbe (Concordia University)
On the Origin of "Floppiness" in Nitrilimine
- 4A Etienne Paradis and Gilles H. Peslherbe (Concordia University)
A Density Functional Theory Investigation of the Structure and Bonding of NO₃⁻, ClO₄⁻, BF₄⁻ Anions in Aqueous Clusters
- 4B Sergei Manzhos and Tucker Carrington (Université de Montréal)
Defeating the Curse of Dimensionality: A Study of the Complexity of a Neural Network Interpolant of a Potential Energy Surface as Function of Dimensionality
- 5A Si-Chuan Xu, James T. Hynes, and Gilles H. Peslherbe (Concordia University)
A Systematic Density Functional Theory Investigation of the Glycine Conformers
- 5B Jean Christophe Tremblay and Tucker Carrington Jr. (Université de Montréal)
A New Iterative Method for Computing the Energies and Lifetime of Resonance States as Applied to HCO
- 6A Sacha Z. Zlatkova and Gilles H. Peslherbe (Concordia University)
Excited-State Ionization of HCl and HBr in Water Clusters
- 6B Denise M. Koch, Qadir K. Timerghazin, Gilles H. Peslherbe (Concordia University), Branka M. Ladanyi (Colorado State University), and James T. Hynes (Ecole Normale Supérieure, Paris, France and University of Colorado)
Photodissociation Dynamics of NaI(H₂O)_n Clusters

- 7A** Pratibha Malla and Heidi M. Muchall (Concordia University)
Structural Analysis of N-Phenyl-N'-Sulfinylhydrazines
- 7B** Daryoush Tahmassebi (Brandon University) and Mohammad Solimannejad (Brandon University and Arak University, Iran)
Theoretical Study of Glycine-Sulfur Trioxide Complex
- 8A** Lei Zhang, Heidi M. Muchall, and Gilles H. Peslherbe (Concordia University)
On a Possible "anti-meta Effect" in Phenol Radical Cations
- 8B** Tao-Nhân V. Nguyen, Qadir K. Timerghazin, Gilles H. Peslherbe (Concordia University) and Holger Vach (Ecole Polytechnique)
Novel Oxidation Process of a Si(100) Surface by (O₂)_n Cluster Impact. Theoretical Evidence for Nonadiabatic Chemistry
- 9A** Dominika Zgid and Marcel Nooijen (University of Waterloo)
Density Matrix Renormalization Group
- 9B** Yin Wei and Gilles H. Peslherbe (Concordia University)
Density-Functional Theory Studies of the Reactivity of Vanadium Oxide Cluster Cations towards Fluorocarbons
- 10A** Xue Feng Wang (Concordia University), B. Molnar (Universiteit Antwerpen, Belgium), P. Vasilopoulos (Concordia University), F. M. Peeters (Universiteit Antwerpen, Belgium)
Square-Wave (Magneto)Conductance through a Chain of Rings Due to Spin-Orbit Interaction
- 10B** Xue Feng Wang and P. Vasilopoulos (Concordia University)
Square-Wave, Spin-Dependent Transmission through Periodically Stubbed Electron Waveguides
- 11A** M.A. Whitehead, T.G. van de Ven, and Thomas Lazzara (McGill University)
Theoretical Investigation and Experimental Characterization of SMI Nanostructures
- 11B** E. Bunce, G.W. vanLoo (Queen's Chemistry), D.C. Churchill (Memorial University of Newfoundland)
Investigations into the Binding of an Organophosphorus Pesticide, Diazinon, with Cyclodextrins
- 12A** Nabil Al-Yassir, Raymond Le Van Mao, and Ngoc Thanh Vu (Concordia University)
Surface Characterization and Catalytic Reactivity of Supported Bimetallic Molybdenum Oxide and Cerium Oxide for the Conversion of Heavy Crude Oils into Light Olefins and Transportation Fuels
- 12B** Lin Lu and Raymond Le Van Mao (Concordia University)
Nano-Structured Mesoporous Materials: Preparation and Characterization of Silica Nanoboxes
- 13A** Sean R. Hughes, John A. Capobianco, and Gilles H. Peslherbe (Concordia University)
A Quantum Chemistry Investigation of the Stability of Eu³⁺(H₂O)_n Clusters with Respect to Deprotonation
- 13B** Philippe Rocheleau, Min Zhuang, François Goyer, David St-Hilaire, Paul Boulanger, Hilke Bahman, Sergey Maximoff, and Matthias Ernzerhof (Université de Montréal)
Modeling the Conductance of Molecular Electronic Devices

TALKS

Stressed-Out Metals: Predicting Their Response from the Bottom Up

Emily A. Carter
Princeton University

Mechanical properties of materials are affected not only by macroscopic external loads, but also by chemical reactions, typically at surfaces and interfaces. For example, impurities in metals often coalesce at grain boundaries, leading to weakening of the sample under stress. Atmospheric chemical corrosion is another example that, when combined with external loads, leads to stress-corrosion cracking. These are inherently multiscale phenomena, where the chemistry occurring at the atomic scale profoundly affects the mechanical properties at the micron to millimeter scale. While ideally characterization of the events involved should be obtained from experiments, in situ characterization is difficult or in many cases not yet possible. We therefore explore what computer simulation techniques can do to help characterize such phenomena.

We are developing two basic strategies of quantum-mechanics-based multiscale modeling, which differ in the way in which the coupling between length scales is accomplished. Either one generates atomic scale information in advance, which then is used to provide the constitutive laws that determine the materials response at the higher length scale, or one directly couples both scales, where on the fly the information from the atomic scale is provided to the macroscopic model, which in turn provides real-time feedback to the atomic scale. Thus far, we are coupling various forms of density functional theory (DFT) at the atomic scale to a finite-element-based continuum mechanics description of the coarser scales. The goal is to develop such simulation tools to the point where they confer *predictive* capability onto engineering models of materials response.

The talk will focus on applications of the first approach to (i) chemically-induced cracking of steel due to hydrogen embrittlement and (ii) shock-induced phase transformations in iron that produce a complex microstructure. In (i), we derive from the atomic scale a universal relation that describes the forces between incipient crack surfaces, which is then used as input to a larger length scale model of fracture. The predicted stress-corrosion cracking behavior of steels is in good agreement with many experimental trends, suggesting that such a model may be useful eventually for determining failure limits of steels. In (ii), we predict the formation of microstructure in iron subjected to compression and shear. We will show that this multiscale model provides insight into discrepancies between various experiments and an explanation for an observed pressure hysteresis loop. The metastable microstructure formed accounts for the latter, while the former is proposed to be due to modest amounts of shear present in the experiments.

State-Selective Internally-Contracted Multireference CC Approach vs. Single Reference CCSD + Extensive Renormalized Triples Corrections

Marcel Nooijen
University of Waterloo

In ab initio quantum chemistry there is a strong preference to use “black box” single reference type of approaches to describe electronic states. Response type of approaches provide similar easy-to-use methods for excited states, which are built on a single reference starting point. These methods can be used to tackle many, but not all problems in electronic structure theory. Exceptions include biradicals, bond breaking phenomena, certain difficult transition states, and most notoriously, many transition metal compounds. For some of these problems multireference methods are indispensable, and it is advantageous to use CC methods, to maintain size-extensivity and to build on the effectiveness of the exponential parameterization in coupled cluster theory. In this way the space of active orbitals can be limited to those orbitals that are vital for a qualitative description of the wave function. I will describe our efforts in this direction. It is also of interest to extend the scope of single reference methods, as it is likely they will always be less ambiguous and more easy to use than multireference techniques. I will describe a modified version of renormalized triple and quadruple corrections, which are fully size-extensive variations of the method of moment Coupled Cluster theory pioneered by Piecuch and Kowalski in recent years.

On-the-Fly Localization of Electronic Orbitals in Car-Parrinello Molecular Dynamics: An Application to the Decomposition of IR Spectra of Aqueous Systems into Solute and Solvent Contributions

Radu Iftimie
Université de Montréal

Mark Tuckerman
New York University

The *ab initio* molecular dynamics formalism of Car and Parrinello is extended to preserve the locality of the orbitals. The supplementary term in the Lagrangian does not affect the nuclear dynamics, but ensures “on the fly” localization of the electronic orbitals within a periodic supercell in the Γ -point approximation. The relationship between the resulting equations of motion and the formation of a gauge-invariant Lagrangian combined with a gauge-fixing procedure is briefly discussed. The equations of motion can be used to generate a very stable and easy to implement numerical integration algorithm. It is demonstrated that this algorithm can be used to compute the trajectory of maximally-localized orbitals, known as Wannier orbitals, in *ab initio* molecular dynamics, with only a modest increase in the overall computer time. We further demonstrate that maximally-localized Wannier orbitals can be used to separate the individual contributions of different molecular species to the linear spectrum of complex systems. The new spectral decomposition method is shown to be useful in present-day *ab initio* molecular dynamics calculations to compute the magnitude of the “continuous absorption” generated by excess protons in aqueous solutions with good accuracy, even when other species present in solution absorb strongly in the same frequency window.

Hydroxyl Radical and Phenol in Aqueous Solution: Computer Simulation

Andriy Plugatyr and Igor M. Svishchev
Trent University

Molecular Dynamics simulations of hydroxyl radical and phenol in water are carried out using a classical SPC/E water model and similar models for hydroxyl radical and phenol. Structural and dynamical properties of hydroxyl radical-water and phenol-water mixtures are studied along the coexistence curve of SPC/E water up to the critical point, and above its critical point with density fixed at 0.3 g/cm^3 . Dramatic change in the diffusion dynamics of water, hydroxyl radical and phenol near the critical point are related to the reorganization of the three-dimensional structure of water, as revealed by the study of the spatial distribution functions. This study helps understand the kinetics of oxidation reactions in high temperature water.

Highly Charged Ions: A Challenge for Density Functional Theory

*Viktor N. Staroverov, Gustavo E. Scuseria,
Rice University, Houston, Texas*

*John P. Perdew, Jianmin Tao,
Tulane University, New Orleans*

*and Ernest R. Davidson
University of Washington*

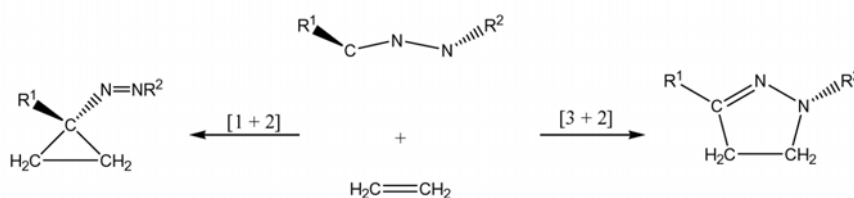
Commonly used density functional approximations can be qualitatively wrong even for relatively simple systems such as highly charged atomic ions. A density functional description of such ions can be improved dramatically by ensuring that: (i) the correlation functional is bounded in the high-density uniform scaling limit; (ii) the exchange functional recovers the correct leading term in the Z -expansion of the exchange energy. Performance of several density functionals that satisfy none, one, or both of these conditions is compared. The best results are obtained with the nonempirical meta-generalized gradient approximation of Tao, Perdew, Staroverov, and Scuseria (TPSS).

Revisiting the 1,3-Dipolar Cycloaddition Mechanism: Nitrilimines as a Case Study

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

After a longstanding controversy about a concerted vs. radical mechanism, it is now firmly established that 1,3-dipolar cycloaddition reactions proceed via a concerted [3+2] mechanism.¹ Nitrilimines, $R^1CN=NR^2$, are 1,3-dipoles that typically undergo such [3+2] cycloaddition reactions. However, in cases where certain geometric constraints are imposed, [1+2] cycloaddition reactions have been observed.² This, combined with the recent assessment of considerable carbene character in the electronic structure of nitrilimines,³ prompted us to explore the competition between the [1+2] and [3+2] cycloaddition pathways. In this work, hybrid density functional theory, PBE0/6-311++G(2df,pd), has been used to examine the two pathways for the reaction of a series of nitrilimines with ethene. Both pathways have only small barriers, all below 14 kcal mol⁻¹, and the potential energy surface in the region of the transition states for the two pathways is rather flat. In the majority of cases the [3+2] path is favoured, sometimes by as much as 7 kcal mol⁻¹. This pathway, however, is typically asynchronous, with formation of the CC bond more pronounced than that of the CN bond in the transition state. These results suggest that carbene character may influence the [3+2] pathway and an alternative mechanism is proposed that explains the unusual regio- and stereoselectivity observed in nitrilimine cycloaddition reactions.

1. Houk, K. N.; Gonzalez, J.; Li, Y. *Acc. Chem. Res.* **1995**, *28*, 81-90.
2. Garanti, L.; Vigevani, A.; Zecchi, G. *Tetrahedron Lett.* **1976**, 1527-1528.
3. Mawhinney, R. C.; Muchall, H. M.; Peslherbe, G. H. *Chem. Commun.* **2004**, 1862-1863.



Theoretical Study of the Hydrolysis of N-Sulfinylamines

*Elena V. Ivanova and Heidi M. Muchall
Concordia University*

N-sulfinylamines (R-N=S=O) are known to hydrolyze readily in the presence of a catalyst.¹ With the quantum chemistry calculations we studied the hydrolysis of N-sulfinylamines with different substituents at amino group (R= H, Me, Ph) in clusters of n (n=1-5) water molecules in gas phase. We found that at least two water molecules are necessary for the reaction to happen. The competition between the reaction across the N=S and the S=O bond and the influence of the substituent R on reactivity were examined. The thermochemistry of the hydrolysis and all reaction intermediates was determined with the B3LYP/6-31+(2d,2p) method, which was found to be the best choice with a basis set superposition error of less than 0.7 kcal/mol for the ternary complexes. We found that the introduction of a third water molecule increases the flexibility of the system,² which leads to decrease of the energetic barrier for hydrolysis. Further increase of the cluster size, up to 5 water molecules, does not have a significant effect on the reaction.

(1) Mironova, D. F.; Konoplya, O. Y. *Ukr. Khim. Zhn.* **1976**, 42, 374-378.

(2) Sicilia, M. C.; Munoz-Caro, C.; Nino, A. *ChemPhysChem* **2005**, 6, 139-147.

A Theoretical Study of Criegee Intermediate Complexes with Water Clusters and its Reactions in the Atmosphere

*Andrew Ryzhkov and Parisa Ariya
McGill University*

Gas-phase reactions with ozone are significant removal process for volatile unsaturated hydrocarbons in troposphere, which also produce atmospherically important species: HO, HO₂, organic and inorganic peroxides. The primary product of the ozonolysis of alkenes is the Criegee intermediate (CI), the most important reaction of which is interaction with water. In present work ab initio and density functional methods were applied to evaluate importance of formation of CI complexes with water clusters for atmospheric reactions. Various structures CI...(H₂O)_n with n=1..4 were calculated and minimal configurations are found. In addition, the reactions of these complexes were investigated; energy barriers were determined. The relative rate constants were calculated, and reaction ratios based on typical water clusters abundances in the atmosphere were estimated. It has been found that water clusters alter reactions of the CI significantly.

An Explanation of the Denaturing of Proteins

Michael Lever

Canterbury Health Centre, New Zealand

Robert G.A.R. Maclagan

University of Canterbury, Christchurch, New Zealand

Cecile Malardier-Jugroot and M.A.Whitehead

McGill University

Using a small amide to model the polypeptide backbone of a protein, ab initio methods were used to show that the denaturing or non-denaturing effects of solutes on proteins is related to the value of the bond dipole. In addition, a complete study of the model protein-solute interactions showed that the interaction with a denaturing solute destroys the model peptide-peptide interaction whereas the interaction with a non-denaturing solute leaves the model peptide-peptide interactions almost unaltered. Consequently the interaction of the solutes with proteins can be explained.

New Tools for Studying the Dynamics of Small Molecules: Ideas and Applications

Tucker Carrington, Université de Montréal

I shall discuss new methods for computing vibrational energy levels of small polyatomic molecules. The principal impediment to the calculation of energy levels is the size of the required basis set. If one uses a product basis the Hamiltonian matrix of a four-atom molecule is too large to store in core memory.

We discuss iterative methods that enable one to use a product basis to compute energy levels (and spectra) without storing a Hamiltonian matrix. Despite the advantages of iterative methods it is not possible, using product basis functions, to calculate vibrational spectra of molecules with more than four atoms. A recent method combining contracted basis functions and the Lanczos algorithm with which vibrational energy levels of methane have been computed is described. New ideas for reducing basis set size by using basis functions that nearly diagonalise the Hamiltonian matrix will also be discussed

Quantum Calculation of Rovibrational Spectra of OCS-He₂, N₂O-He₂ and CO₂-He₂

Xiaogang Wang, Tucker Carrington Jr., J. Tang, and A.R.W. McKellar
Université de Montréal

The system of a linear dopant and two He atoms is interesting because it is related to the solvation of the dopant in He nanodroplet. The rovibrational spectra of Van der Waals complexes OCS-He₂, N₂O-He₂ and CO₂-He₂ are calculated variationally using a direct product basis and a Lanczos eigensolver. We have taken into account all the inter-molecular degrees of freedom and the overall rotation. Of particular interest is the torsional motion of the two He atoms around the linear dopant. We have found that the rotational constants are very different for different excited torsional states, and that the normally "forbidden" transitions between different torsional states could be observed due to rovibrational couplings. This study turns out to be very helpful in assigning the experimental infrared and microwave spectra in pulsed supersonic jet expansion.

**How to Choose 1-D Basis Functions so that a
Very Efficient Multidimensional Basis may be Extracted
from a Direct Product of the 1-D Functions:
Energy Levels of Strongly Coupled Systems with
as many as 16 Coordinates**

*Richard Dawes and Tucker Carrington Jr.
Université de Montréal*

We propose a new scheme for choosing basis functions for quantum dynamics calculations. Direct product bases are frequently used in quantum dynamics calculations. The number of direct product functions required to converge a spectrum, compute a rate constant etc is so large that direct product calculations are impossible for molecules or reacting systems with more than four atoms. It is common to extract a smaller working basis from a huge direct product basis by removing some of the product functions. We advocate a build and prune strategy of this type. The 1-D functions from which we build the direct product basis are chosen to satisfy two conditions: (1) they nearly diagonalize the full Hamiltonian matrix; (2) they minimize off-diagonal matrix elements that couple basis functions with diagonal elements close to those of the energy levels we wish to compute. By imposing these conditions we increase the number of product functions that can be removed from the multidimensional basis without degrading the accuracy of computed energy levels. Two basic types of 1D basis functions are in common use: eigenfunctions of 1D Hamiltonians and discrete variable representation (DVR) functions. Both have advantages and disadvantages. The 1-D functions we propose are intermediate between the 1D eigenfunction functions and the DVR functions. If the coupling is very weak they are very nearly 1D eigenfunction functions. As the strength of the coupling is increased they resemble more closely DVR functions. We assess the usefulness of our basis by applying it to model 6, 8, and 16D Hamiltonians with various coupling strengths. The applicability of perturbation theory in the derived basis is also discussed.

Constrained Semiclassical Molecular Dynamics

Bilkiss Issack and Pierre-Nicholas Roy
University of Alberta

We have developed a general method to study the dynamics of constrained molecular systems based on the Semi Classical Initial Value Representation (SC-IVR). An interesting feature of the approach is that the calculations are performed in Cartesian coordinates. The method is centered on the computation of an autocorrelation function and its Fourier transform which yields the eigenstates of the system. We treat the constraints by projecting out undesired motions from the Hessian of the system. To test our approach, the Zero Point Energies (ZPEs) of three constrained argon trimers were determined from semiclassical dynamics performed at different levels of approximation. The results are compared to the corresponding exact ZPEs. We observe the expected increase in ZPEs with increasing vibrational number of degrees of freedom. We also find a good agreement between the semiclassical results and the exact energies for all three test systems.

Molecular Theory of Transport Properties of Liquid Carbon Dioxide

Afshin Eskandari Nasrabad, Rozita Laghaei, and Byung Chan Eu
McGill University

Modified free volume theory and the generic van der Waals equation of state are used to calculate the density and temperature dependence of the self-diffusion coefficient of carbon dioxide with the help of a Monte Carlo simulation method for the pair correlation function. A Lennard-Jones site-site interaction potential model is used to model the molecular carbon dioxide. The self-diffusion coefficient is examined at four different isotherms and isobars. The self-diffusion coefficients so computed have been made use of to compute the viscosity of carbon dioxide by applying the density fluctuation theory formula for viscosity, which is given in terms of the self-diffusion coefficient among other molecular quantities. The theoretical self-diffusion coefficient and viscosity are found to be in excellent agreement with experimental data available in the literature. Therefore we are now in possession of a long sought molecular theory of transport coefficients that can account for the density and temperature dependence in terms of intermolecular potentials.

IR Shifts of SF₆ in an Ar Matrix and Fitting Spectra Utilizing a Genetic Algorithm

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An infrared active polyatomic molecule has several vibrational modes, each of which has a characteristic frequency. If the molecule is trapped in a matrix of perturbing atoms, the frequencies will change, giving rise to frequency shifts in the vibrational spectrum, and if the vibrational mode is degenerate, the perturbation may break the degeneracy. Our simulations examine a model for the triply degenerate ν_3 mode of SF₆ trapped in an Ar matrix. Monte Carlo simulations are used to find the most stable configuration of the SF₆ and surrounding Ar atoms, and perturbation theory is used to calculate the frequency shifts. Different trapping sites are found to have distinctly different spectra. Our final objective is to determine what combination of sites is responsible for the observed spectrum. Since the peaks in the observed spectra cannot be assigned a priori, we plan to use a Genetic Algorithm to fit those peaks.

Thermodynamics of Surface vs. Interior Solvation in Halide-Water Clusters

*Denise M. Koch and Gilles H. Peslherbe
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It is now well established that large halide ions tend to sit at the surface of small- to medium-sized water clusters. One of the fascinating features of these surface solvation cluster structures lies in the possibility of photochemical transfer of an electron from the ion to the solvent, giving rise to so-called charge-transfer-to-solvent (CTTS) excited states, which eventually lead to precursor states of the solvated electron. 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 $X^-(H_2O)_n$ clusters ($X^- = F^-, Cl^-, Br^-, I^-$, $n=12-64$) from first-principles molecular dynamics and Monte Carlo calculations, and classical 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 the smaller water clusters, but 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 these cluster sizes. From the first-principles calculations, we will attempt to connect our calculated results to experimentally-determined vertical detachment/excitation energies as a function of cluster size. Finally, the relative merits of first-principles simulations vs. simulations with non-polarizable and polarizable model potentials will be discussed.

Potential Energy Surfaces and Dynamics of the Charge-Transfer-To-Solvent (CTTS) and Ionized States of Iodide-Acetonitrile Clusters

*Qadir K. Timerghazin and Gilles H. Peslherbe
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One of the fascinating features of clusters made up of a halide ion and a number of polar solvent molecules lies in the possibility of photochemical transfer of an electron from the anion to the solvent, giving rise to so-called charge-transfer-to-solvent (CTTS) excited states, which eventually lead to cluster precursors of the solvated electron. In this contribution, we report quantum-chemical studies of the potential energy surfaces of the CTTS and ionized states of small halide-solvent clusters for prototype iodide-acetonitrile complexes. Applications of the calculated potential energy surfaces to the studies of the dynamics of the CTTS states are discussed in connection with recent experimental ultra-fast photoelectron spectroscopy results.

Using Nitrogen Base Cyclic Motifs as RNA Building Blocks

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To improve RNA three-dimensional structure prediction and modeling, we performed a systematic study of the interactions between the nucleotides in the X-ray crystallographic structure of the large ribosomal subunit of *Haloarcula marismortui*. The results revealed an unsuspected structural organization consisting of a number of short, indivisible and recurrent nucleotide interaction cycles that are themselves connected at a higher level through hub cycles. Here we show how such cyclic motifs in the large ribosomal subunit were systematically identified and classified. Two motifs were selected for further analyses: the much studied GNRA tetra-loop and the GNRA i-loop, a motif similar to GNRA tetra-loops, but forming in interior loops. We show that GNRA tetra-loops are not restricted to the GNRA sequence. The discovery of an RNA stereochemistry forming hub networks of stable cycles of nucleotide interactions represents a new theoretical foundation on which to base the development of new RNA structure approaches.

Bioinformatics and Its Application on Inhibitor Design Against SARS

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After a brief introduction of bioinformatics is given I shall present some of our recent works on the development of drugs against severe acute respiratory syndrome (SARS). Studies of docking KZ7088(a derivative of AG7088) and the AVLQSGFR octapeptide to the SARS coronavirus main proteinase (Mpro or 3CLpro) were conducted. It has been observed that both compounds interact with the active site of the SARS enzyme through six hydrogen bonds. The octapeptide AVLQSGFR was synthesized, then the antiviral potential of the octapeptide against SARS coronavirus (BJ-01) was assessed. The results demonstrate that AVLQSGFR is the most active in inhibiting replication of the SARS coronavirus compared with other compounds reported so far, while no detectable toxicity on Vero cells under the condition of experimental concentration is observed.

A pharmacophore search was conducted over 3.6 millions of compounds based on the atomic coordinates of the complex obtained by docking KZ7088 (Chou, K.C., Wei, D.Q., and Zhong, W.Z.: *Biochem. Biophys. Res. Commun.* 2003, 308, 148-151). It has been found that, of the 3.6 millions of compounds screened, 0.07% are with the score satisfying five of the six pharmacophore points. Moreover, each of the hit compounds has been evaluated for druggability according to thirteen metrics based on physical, chemical and structural properties. Of the 0.07% compounds thus retrieved, 17% have a perfect score of 1.0, while 23% with one druggable rule violation, 13% two violations, and 47% more than two violations. If the criterion for druggability is set at a maximum allowance of two rule violations, we obtain that only about 0.03% of the compounds screened are worthy of further tests by experiments. The cleavage mechanism of SARS Mpro for octapeptide AVLQSGFR is studied using molecular mechanics

(MM) and quantum mechanics (QM). The catalytic dyad His-41 and Cys-145 in the active pocket between domain I and II seem to polarize the π -electron density of the peptide bond between Gln and Ser in the octapeptide, leading to increases of positive charge on C(CO) of Gln and negative charge on N(NH) of Ser. The possibility of enhancing the chemical bond between Gln and Ser based on “distorted key” theory is examined. The scissile peptide bond between Gln and Ser is found to be solidified through “hybrid peptide bond” by changing the carbonyl group CO of Gln to CH₂ or CF₂. This leads to break the π -bond system for the peptide bond and make the octapeptide (AVLQSGFR) a “distorted key” and a potential starting system for the design of anti SARS drugs.

Mutation Miner - Textual Annotation of Protein Structures

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Protein structure visualization tools render images that allow the user to explore structural features of a protein. Context specific information relating to a particular protein or protein family is not easily integrated and must be uploaded from databases or provided through manual curation of input files. We describe a mixed natural language processing and protein sequence analysis approach for the retrieval of mutation specific annotations from full text articles for rendering with protein structures.

Ca²⁺ Binding to Calbindin D28K: A Molecular Dynamics Study

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Calcium is widely used in biological systems as a regulator of physiological functions. Calbindin D28k is an EF-hand Ca-binding protein of unknown structure found in the brain, kidney and intestine. The goal of our research is to determine the 3-D structure of calbindin D28K in the Ca-free and Ca-loaded forms using molecular mechanics with distance constraints obtained from intramolecular cross-linking and mass spectrometry. Molecular dynamics simulations are being used to investigate the six putative EF-hand domains designated EF1, EF2, EF3, EF4, EF5 and EF6 in the protein. Our initial emphasis is on the role played by Ca in the stabilisation of isolated Ca-free and Ca-loaded EF-hand domains. Reported spectroscopic (CD and NMR) data(1) show that five of the six peptides corresponding to the isolated EF-domains bind Ca (EF1, EF3, EF4, EF5 and EF6). EF1, EF3, EF4 and EF5 possess the consensus sequence for Ca binding (2) but EF2 and EF6 disagree with this sequence in X-Y residues. In contrast to the observed data, our preliminary molecular dynamics results show that EF2 binds Ca when Na counterions are included in the simulation. Preliminary QM/MM molecular dynamics simulation that characterise the interaction between Ca and the amino acid residues in the binding loop also will be presented.

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Computational Investigations on Biochemical Catalysis

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Biological catalysts enable the reactions essential for life to occur at biologically viable rates under relatively mild conditions. This is achieved through the co-operative effects of various substrate-catalyst interactions. Until quite recently, all such catalysts were believed to be proteins, in some cases containing additional functional prosthetic groups, e.g., heme. However, it is now known that ribonucleic acids (RNA) may also form catalytically active species and that, furthermore, these ribozymes often catalyse the same reactions as protein enzymes. While experimental investigations have provided considerable insight into how biological catalysts function, they often encounter difficulties. These can include not only identification of possible mechanism intermediates, but also elucidating how the substrate may actually be bound. We employ computational chemistry in order to gain a greater understanding of how such catalysts function. In particular, we are interested in the ribosome ribozyme, the site of protein formation in cells, and nitric oxide synthase. Some recent results of our investigations on these two biocatalysts will be presented and discussed.

3,5-Dihydroxybenzylalcohol Based Dendrimers: Structure Evaluation and Molecular Encapsulation in Generations 1-5

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Theoretical calculations using Molecular Mechanics MM+ method and the PM3 Semi-Empirical Molecular Orbital Theory were used to optimize the structures of 3,5-dihydroxybenzyl alcohol (DHBA) based dendrimer generations 1 to 5 (DG1-5). DG1-3 have a relatively open structure with no internal spaces of any particular size or shape. DG4 and 5 assume a more globular structure with well-defined internal cavities. Encapsulation of Disperse Red 1 (DR1) into the cavities of these dimethylsilyl linked DHBA based dendrimers, before and after aggregation, led to a blue shift in the λ_{max} of DR1, and Transmission Electron Microscopy (TEM) showed a rectangular shape of dendritic aggregates containing DR1. Catalytic activity of (COD)RhCl(PPh₂(CH₂)₃OH) encapsulated in dendritic aggregates below and above critical aggregation concentration (cac) of generations 1-4 was examined. A significant decrease in catalytic conversion of 1-decene to decane in dendrimer generations 4 upon going from a concentration below cac to above cac was observed.

A Density Functional Study of the Hydrogen-Bond Network within the HIV-1 Protease Catalytic Site Cleft

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The relative energy between two different protonation sites of the Asp25' catalytic site residue is computed and analyzed for various HIV-1 Protease/inhibitor complexes and compared to the wild-type structure. By comparing calculations of negatively charged fragments of gradually increasing size up to 105 atoms we show that correct modeling of the HIV-1 Protease active site requires much larger models than the commonly used acetic acid/acetate moieties. The energy difference between the two proposed protonation sites decreases as the size of the system increases and tends to converge only when the entire catalytic triad of both monomers is taken into account. The importance of the Gly27 backbone amine groups in the stabilization of the negative charge within the catalytic site cleft is revealed. Comparison of the wild-type structure with the structures from various Pr/drug complexes indicates that the HIV-1 protease has a particular catalytic site flexibility.

Probing Hydrophobic Association and Protein-Ligand Binding with Free Energy Simulations in Four Spatial Dimensions

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Novel computational techniques for the calculation of excess chemical potentials and binding free energies in full-atomic systems of biological scale are explored. An imaginary fourth spatial dimension is introduced as a computationally efficient means of turning on or turning off non-bonded interactions. Molecular simulations are used to compute the potential of mean force (PMF) acting on the molecule of interest in the fourth dimension. The method is applied (1) to study the thermodynamic basis for the effect of guanidium hydrochloride, a protein denaturant, on hydrophobic association and (2) to the calculation of the absolute binding free energies of benzene and other ligands to a variant of T4 Lysozyme. Results are corrected for standard state conditions and compared directly to experimental measurements.

A Quantum Chemical Analysis into the Stabilizing Interactions in Nucleic Acid Base Pairs

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Quantum chemical calculations have been used extensively in the study of base pair interactions.¹ However, fully optimized base pairs in the gas phase may not be the best representatives of experimentally observed base pair geometries and base interactions such as those found within RNA bulge and loop structures. Our aim is to be able to understand and accurately quantify the interactions that stabilize these less known motifs. As a first step towards this goal, we analyzed base pairs from two well known nucleic acid structures (a B-DNA and an A-RNA helix). Maintaining the experimental geometry of each base pair, we obtained wavefunctions with the B3LYP/6-31G(d,p) model chemistry and analyzed the topology of the electron density in the intermolecular area with the Quantum Theory of Atoms in Molecules.² Fully optimized base pairs were analyzed for comparison. All intermolecular interactions were identified as hydrogen bonds according to the criteria proposed by Popelier and Koch.³ Our results show that the hydrogen bonding patterns vary substantially with the observed geometry of the experimentally derived base pairs.

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POSTERS

Molecular Simulations Performed with Collagen Monomer Model

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Collagen is an abundant extra-cellular protein with a unique triple helical structure and an ability to self-assemble into several different aggregates. Understanding of this process has been impeded by the lack of a complete 3D structure, which is impossible to obtain using current experimental techniques. Therefore, a model of human type I collagen was created from a statistical analysis of previously solved structures combined with CHARMM force field structural information. Minimization was performed using molecular mechanics and dynamics simulations both in-vacuo and with water as solvent. The final structure provides information about detailed geometry of the monomer unit and other characteristics including bulk properties and surface charge distribution.

Internally Contracted State-Selective Multi-Reference Methods Based on Equation-of-Motion Coupled-Cluster Approach

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Quasi-degenerate situations are an ubiquitous phenomena in electronic structure calculations involving stretched geometries, transition states, open-shell molecules, and excited states. These situations often call for a combination of multi-reference description of non-dynamical correlation and powerful coupled-cluster description of dynamical correlation effects. The poster starts by highlighting some of the well-known deficiencies of effective Hamiltonian based multi-reference coupled-cluster methods. Different multi-reference paradigms are presented with a comparison of their strengths and weaknesses. In the recent years, state-specific multi-reference methods have emerged as viable alternatives. Specifically, we discuss one such method similar in structure to the Equation-of-Motion coupled-cluster method. Some applications and ongoing developments are pointed out.

Halide Ions in a “Methyl Pocket”: Competition between Hydrogen Bonding and Ion-Dipole Interactions

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The ability of C-H bonds to participate in hydrogen bonding has been an issue of long-standing interest. In the literature, the proposed nature of the interaction between substituted methanes RCH_3 and halide ions ranges from purely electrostatic, ion-dipole attraction to regular or improper, blue-shifting hydrogen bonding. The situation is especially unclear in the case of halide-acetonitrile complexes and clusters, since several reported theoretical and experimental studies disagree on the prevalent role of either ion-dipole interactions or hydrogen bonding. In this contribution, we will present a detailed systematic computational study of the structures, binding energies and potential energy surfaces for the series of small halide-acetonitrile clusters $X-(CH_3CN)$. The applicability of various quantum-chemical methods to the systems of interest will be discussed and the nature of the bonding interactions in the $X-(CH_3CN)$ complexes will be analyzed using the Atoms-In-Molecules and Natural Bond Orbitals approaches. In light of this computational study, possible explanations for recent cluster and bulk solution experimental results and existing theoretical models will be critically discussed.

Poster: 2B

Computational Studies of Agostic Interactions between Substituents on the Cyclopentadienyl Ring and the Metal in Zirconocenium Complexes

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Many processes, catalyzed by organometallic complexes, involve agostic-type interactions between ligands and transition metal cations. For example, agostic interactions in zirconocenium cationic complexes, which are believed to be the active catalytic species for α - olefin coordination polymerization, play a key role in governing the reactivity of the catalyst and the resulting polymeric structure.¹ In this work, we are interested in the possible agostic interactions between flexible alkyl-like substituents placed on the cyclopentadienyl ring and a metal center in model zirconocenium cationic species: $[\text{Zr}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Me}]^+$, R = H, Me, *t*-Bu, $(\text{CH}_2)_n\text{CH}_3$, SiMe₃. Our aim is also to understand the driving forces behind the agostic-type interactions. A combination of theoretical methods, such as the density functional theory with the natural bond orbital analysis and the quantum theory of atoms in molecules,² is used to explore these issues. We report results of calculations for zirconocenium complexes with various substituents (R), varying the number of carbon atoms in the hydrocarbon chain ($n = 1\text{-}3$). We examine the structures, energetics and electron density distributions for the different species, focusing on the factors that are responsible for the formation of agostic interactions, and we also discuss the nature of these interactions.

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A Computational Study of the Unimolecular C₂ Fragmentation of the C₈₂ Fullerene

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Although fullerenes are known to have a remarkable kinetic stability, energetic characteristics of their C₂ fragmentation are still a controversial topic in the literature [1, 2]. In this work, we address the unimolecular C₂ fragmentation of three C₂ and three C_s isomers of C₈₂ by means of semiempirical (PM3), ab initio (HF/STO-3G) and density functional theory (B3LYP/3-21G, B3LYP/6-31G*) methods. The fragmentation of the most thermodynamically stable isomer of C₈₂, C₂(**3**), was investigated through both the Stone-Wales (SW) transformation and via 7-membered-ring isomer formation, whereas the fragmentation of other, less stable, C₈₂ isomers was considered only through the more energetically favorable SW pathway.

At the most reliable level of theory employed here (B3LYP/6-31G*), the C₂ fragmentation energies of the most stable C₂ (**3**) isomer of C₈₂ were found to lie in the range of 9.3 – 9.6 eV, which is 0.7 – 1.1 eV larger than recent experimental data [3, 4]. These results may suggest that other isomers, with lower fragmentation energies, may be present in sufficient amounts in experimental samples. The influence of basis set extension on resulting fragmentation energies calculated within density-functional-theory framework and empirical corrections to fragmentation energies will be discussed.

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On the Origin of “Floppiness” in Nitrilimine

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The recent success of the Huygen space probe will probably result in renewed interest in small nitrogen-containing molecules, such as CNN and HCNN, as they have been implicated in the chemistry of Titan’s atmosphere.¹ The focus of our current research is nitrilimine, HCNNH, a small nitrogen-containing molecule, whose defining properties include its “floppiness”, or soft bending potential, where two coupled vibrations link two stationary points of similar energy.² One of the precursors of nitrilimine, the diazocarbene radical, :CNN, exhibits a Renner-Teller splitting, which lifts the degeneracy of the two bending vibrations.³ Further, the negative ion photoelectron spectrum of HCNN⁻ reveals a complexity that implies that the ionized species, HCNN[·], also a precursor of nitrilimine, is a wide-amplitude bender, or “floppy”, molecule. This suggests that the soft bending potential of nitrilimine may be a result of these features in the precursor systems. To examine this issue, the various electronic states of CNN, HCNN, CNNH and HCNNH have been examined using conventional density-functional theory, PBE0/6-311++G(2df,pd). The geometries, vibrational frequencies, and excitation energies for these systems will be presented and the relationship between the Renner-Teller splitting in CNN and the “floppiness” in nitrilimine will be explored.

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A Density Functional Theory Investigation of the Structure and Bonding of NO_3^- , ClO_4^- , BF_4^- Anions in Aqueous Clusters

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The structure of hydrated molecular anion clusters is investigated with density functional theory. The optimized structures of $\text{NO}_3^-(\text{H}_2\text{O})_n$ $n=1-6$, $\text{ClO}_4^-(\text{H}_2\text{O})_n$ $n=1-8$ and $\text{BF}_4^-(\text{H}_2\text{O})_n$ $n=1-8$ are obtained with B3LYP/6-311+G**, B3LYP/aug-cc-pVDZ, BP86/DZVP and PLAP/DZVP along with hydration energies, enthalpies and vibrational frequencies. The structures obtained suggest that hydrogen bonding play an important role in stabilizing the cluster. The calculated hydration enthalpies correlate well with experimental data, and the vibrational analysis shows a red shift of the O-H vibration frequency, in agreement with infrared spectroscopy results. Ion-solvent and solvent-solvent hydrogen bonds are then characterized by natural bond orbital (NBO) analysis and with the quantum theory of atoms in molecules (AIM). The ion-solvent hydrogen bond is found to be much weaker than the water-water bond in $\text{ClO}_4^-(\text{H}_2\text{O})_n$ and $\text{BF}_4^-(\text{H}_2\text{O})_n$ cluster anions, as suggested by experimental spectroscopy results. A correlation between bond order, electronic density and bond length is observed for hydrogen bonds.

Defeating the Curse of Dimensionality: A Study of the Complexity of a Neural Network Interpolant of a Potential Energy Surface as a Function of Dimensionality

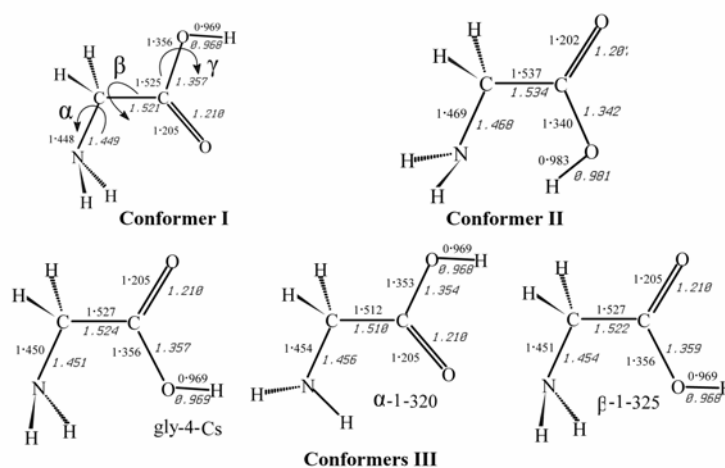
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We consider the problem of interpolation of a function - such as a molecular potential energy surface - known at a number of configurations from ab initio calculations. We use Neural Networks (NN's) to build interpolation functions. NN's have been proven to be universal function approximators and have been used for curve fitting and, specifically, molecular potential fitting, for modeling of kinetic equations as well as for the solution of Schrödinger equation. The method permits an uneven distribution of data points, needed to emphasise dynamically important regions of configuration space, and there are indications that NN's may not be subject to the curse of dimensionality. While other workers have studied particular problems, we present a consistent study of scaling properties of NN's with problem dimensionality. We build optimised networks to fit model potentials of increasing dimensionality to a given tolerance and show that the number of network nodes and weights grows slowly with problem dimensionality and the size of the data set. We also report favourable interpolation properties of NN interpolants.

A Systematic Density Functional Theory Investigation of the Glycine Conformers

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Density Functional theory, B3LYP/6-311+G(d,p) in particular and MP2 as well, has been used to map the potential energy surface of glycine over three internal rotational degrees of freedom in order to accurately and systemically characterize all glycine conformers. This work is motivated by the possible role of glycine conformers in protein structure and the search for the glycine molecule in the interstellar medium in the context of astrobiology.¹ From the potential energy surfaces, a total of fourteen minimum-energy glycine conformers are found; among the fourteen, ten conformers possess C₁ symmetry (five pairs of mirror-image-symmetry configurations), and four conformers possess C_s symmetry. The present work provides support that the second most stable Conformer II possesses C₁ symmetry (unplanar form), while the planar form of C_s symmetry is a transition state connecting a pair of mirror-image Conformers II. Conformers II are 0.8 kcal/mol higher in energy, relative to the most stable Conformer I. Conformer I and Conformers II most likely co-exist since the energy barrier for interconversion is 8 kcal/mol high. Further, the third most stable Conformers III of glycine include three conformers named gly-4-C_s, α -1-320 and β -1-325 (the later two representing pairs of mirror image C₁-symmetry configurations). Conformers III are 1.5 kcal/mol higher in energy, relative to conformer I, with energy barriers for interconversion estimated to be 1.5~2.0 kcal/mol high. The present systematic investigation of glycine conformers yields a total of 14 conformers in contrast to the 8 conformers reported in the literature;² and clarifies some issues about the third most stable configurations and symmetry in glycine conformer.^{3,4}



A New Iterative Method for Computing the Energies and Lifetime of Resonance States as Applied to HCO

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Resonances are metastable states embedded in the continuum. Their associated energies and lifetimes can be computed by adding a complex absorbing potential to the Hamiltonian. Following Mandelshtam and Neumaier, we use a special energy-dependent absorbing potential and solve the time-independent Schrödinger equation. This is done by computing eigenvalues of a real asymmetric matrix U with complex eigenvalues distributed inside the unit circle in the complex plane. There exists a simple map between eigenvalues of the matrix U and energies and lifetimes of the resonances. The coupled-two term variant of the two-sided Lanczos algorithm is used to extract approximate eigenvalues of the matrix U . The eigenvectors associated with these approximate eigenvalues are then used as a basis for the accurate calculation of energies and wave function of the resonance states. The method is applied to the resonances of HCO. We compare properties of the method with those of established approaches.

Excited-State Ionization of HCl and HBr in Water Clusters

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The ionization of strong acids HX (X=Cl, Br) in the presence of water in the ground and excited electronic states is considered a key step in processes leading to atmospheric ozone depletion. Experimental investigations of acid dissociation ($H^+ + X^-$) and hydration of ion pairs ($X^-(H_2O)_nH_3O^+$) at the molecular level are hindered by instrument limitations¹, and to date, theoretical studies address the mechanism of acid ionization in polar and non-polar solvent only partially. In this contribution we look at possible effects of water on the ionization of HCl and HBr in their electronically excited state. We first obtained electronic structures and excited-state potential energy curves of HCl and HBr in the gas phase from CASSCF calculations, along with dipole moments and adiabatic vertical excitation energies. The latter are found in good agreement with previous results^{2,3}. We are currently exploring the influence of water molecules on the excited state HCl and HBr electronic structure and potential energy curves, in order to address the feasibility of excited-state ionization, and possibly photoionization.

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Photodissociation Dynamics of NaI(H₂O)_n Clusters

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We present a theoretical study of the photodissociation dynamics of NaI(H₂O)_n [n=1-4] clusters. The NaI system has been a prototype system for the study of photodissociation dynamics involving curve crossing of covalent and ionic states. A semiempirical valence-bond approach is employed to describe the electronic structure of NaI, while classical potentials are used for the water-water and ion-water interactions. The cluster photodissociation dynamics, including possible nonadiabatic transitions between the NaI excited and ground electronic states, are simulated with the “molecular dynamics with quantum transitions” method. We show that the excited state population decays faster with increasing cluster size, because of the dynamical stabilization of the outer, ionic branch of the excited state potential by solvent molecules. However, 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, such that the water molecules do not significantly affect the NaI photodissociation dynamics beyond the first crossing point. We discuss various possible probe schemes and photoelectron spectra in order to monitor the cluster photodissociation in time and make a connection with experiment.

Structural Analysis of N-Phenyl-N'-Sulfinylhydrazines

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N-phenyl-N'-sulfinylhydrazine (PhNHNSO) is known to form dimers in the solid.^{1,2} However, recent experimental studies have shown that ortho substituted PhNHNSO do not dimerize but meta and para substituted PhNHNSO dimerize.³ Our research interest lies in the rationalization of the observed phenomena of dimerization. In this study, we performed a computational investigation to determine the possible factors that influence the dimerization. A combination of B3LYP/6-31+G(d) and the theory of atoms in molecules (AIM) are used to predict the effect of the nature and the position of substituents on the energetical, geometrical and topological properties of monomers and dimers. The present analyses suggest that substituent in ortho position lead to energetically less stable monomers as well as dimers, whereas, meta and para substitution has only small effect on monomer and dimer stability. The topological analyses of the electron density reveal that the observed N-H---O and C-H---O interactions are not greatly influenced by meta and para substituents. In contrast, ortho substituents greatly influence the N-H---O interactions, and ortho dimers show weaker intermolecular interactions than the other dimers. Based on the obtained results, it is evident that dimerization of ortho substituted PhNHNSO monomers is unfavorable which is consistent with the experimental results.

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Theoretical Study of Glycine-Sulfur Trioxide Complex

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The substantial importance of non-covalent intermolecular interactions in practically all areas of contemporary chemical physics has been demonstrated in different systems (1). From a fundamental point of view, the "Van der Waals molecules" formed by the non-covalent interactions are significant in their own right, as they bridge the gap between the free molecular systems and the corresponding condensed phases they form. From purely applicative aspect, the non-covalently bonded molecular clusters are of certain practical importance in many areas of applied science, such as atmospheric chemistry, catalysis, as well as in biochemically relevant processes. Recently theoretical studies of non-covalently bonded complexes of SO_3 with HX ($\text{X}=\text{F}, \text{Cl}, \text{Br}$) (2), CH_3X ($\text{X}=\text{F}, \text{Cl}, \text{Br}$) (3), HO_2 (4), CO_4 (5), HCN and CH_3CN (6), H_2O (7) and $(\text{H}_2\text{O})_{n=1-3}$ (8) and so many other species have been reported in the literature. To the best of our knowledge, the formation of the complex of sulfur trioxide with HOX ($\text{X}=\text{F}, \text{Cl}, \text{Br}$) has not yet been determined theoretically or experimentally. This has motivated search for the structure and stability of the complexes formed as a result of the bonding between a strong Lewis acid such as SO_3 and Lewis base such as glycine. Among 13 reported conformations for glycine (9), the top seven most stable conformations have been selected and optimized at MP2/6-31+G(d) level. Then the complexation of these seven different conformations with SO_3 were studied at the same level of theory. In each case all of the possible Lewis acid-base donor-acceptor complexes between glycine and SO_3 were investigated and totally 17 different complexes, which are all local minimum, were optimized. The results of these optimization and AIM studies will be presented.

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On a Possible “anti-meta Effect” in Phenol Radical Cations

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The meta effect has been observed as early as 1956 [1] and has been studied intensively in order to understand the unexpected reactivity of meta-substituted benzenoid compounds in photochemical reactions. For example, the meta-nitrophenyl phosphate ester underwent a facile photochemical hydrolysis while the para isomers showed no greater reactivity than in the dark. The meta effect has been ascribed to an increased electron density at the meta-substituted positions in the excited singlet state of benzenoid compounds. A meta-substituent effect has been observed experimentally in the absorption spectra of phenol radical cations [2], but its origin is not known. To that effect, excitation energies of the low-lying excited states of mono and disubstituted methoxy- and methyl-substituted phenol radical cations have been characterized with the Complete Active Space SCF theory (CASSCF), and changes in the atomic point charges upon excitation have been analyzed. While the meta effect is caused by an increased electron density at the meta-substituted position in the excited singlet state of benzenoid compounds, a decreased electron density is observed at the meta-substituted positions in the excited state of phenol radical cations. This may result in changes of orbital energy level which may cause the observed spectral red shift of meta-substituted phenol radical cations. This opposite effect is tentatively called the anti-meta effect.

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Novel Oxidation Process of a Si(100) Surface by $(\text{O}_2)_n$ Cluster Impact. Theoretical Evidence for Nonadiabatic Chemistry

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Recent experimental results show evidence for a completely new oxidation process of silicon surfaces with an $(\text{O}_2)_n$ cluster beam [1]. It was suggested that the reaction is cluster-catalyzed and proceeds via ground-state surface oxidation by molecular oxygen [1]. This assumption has been tested by a molecular dynamics study of $(\text{O}_2)_n$ surface scattering. Our results suggest that O_2 molecules do not gain enough internal energy at surface impact to overcome the activation barrier of the molecular oxidation channel. We thus investigate an alternate pathway that implies a collision-induced, non-adiabatic oxidation mechanism, as molecular dynamics simulations of $(\text{O}_2)_n$ scattering suggest most O_2 molecules gain sufficient internal energy at surface impact to undergo electronic excitation, and excited-state singlet O_2 is a notorious strong oxidant [2]. Multireference quantum chemistry calculations of $(\text{O}_2)_n$ model clusters support the idea that electronic transitions that are in principle forbidden are possible because of curve-crossing and spin-orbit coupling effects in clusters. We will discuss how our model cluster results suggest that cluster size has a catalytic effect on the reaction efficiency, and collision-induced nonadiabatic dynamics may play a major role in the chemistry with a hammer [3].

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Density Matrix Renormalization Group

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In modern quantum chemistry the quest for a general method which can capture cases where mean-field theory breaks down is still of high importance. Currently available methodologies like CASSCF (CASPT2) and MRCI are limited to relatively small active spaces. “The state of the art” which is Full Configuration Interaction fulfills all needed criteria but is much too expensive to be an affordable method for standard quantum chemistry calculations. Different branches of ab initio methods like Coupled Cluster are incapable to describe in a satisfying way the non-dynamic correlation. Multi-reference methods have their share of problems and cannot be used with large active spaces. It has been shown that the Density Matrix Renormalization Group Method is suitable to incorporate non-dynamic correlation, and it has a promising scaling. We are developing a DMRG for multi-reference problems in large active orbital spaces. DMRG has been particularly successful in applications to 1D model systems, that are characterized by localized orbitals and sparse Hamiltonian matrix elements. We can capitalize on these aspects also in applications to molecules by using localized orbitals. The localized orbitals also allow us to treat parts of molecules as domains, which can be improved separately, and this makes the methodology more efficient. We will present preliminary results for DMRG for model systems and small molecules. We discuss the size-consistency of the method with localized orbitals for non-interacting systems. We show how the sparsity of the Hamiltonian matrix in a localized basis can be exploited in DMRG. Finally, we discuss the possible reformulation of the DMRG method.

Density-Functional Theory Studies of the Reactivity of Vanadium Oxide Cluster Cations towards Fluorocarbons

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The structure of $V_2O_4^+$ clusters and the mechanism of their reactions towards CH_2F_2 and CH_3CF_3 have been investigated through density-functional theory (DFT) with the B3LYP/TZVP model chemistry. The association of $V_2O_4^+$ with fluorocarbons to form ion-molecule complexes is a thermodynamically favorable process, which is governed by the formation of V-F bonds, and charge distributions of the cluster ions and fluorocarbons do not change significantly upon complexation. In the reaction of $V_2O_4^+$ with CH_2F_2 , transfer of the terminal oxygen atom along with abstraction of fluorine atoms leads to the stable products $V_2O_3 \cdot F_2^+$ and CH_2O , while transfer of the bridged oxygen atom results in the formation of a stable $V_2O_4 \cdot CH_2F_2^+$ product complex. In contrast, a stepwise HF abstraction is observed in the reaction of $V_2O_4^+$ with CH_3CF_3 . Oxygen transfer in the reaction of $V_xO_y^+$ with CH_2F_2 requires the cleavage of a V-O bond, and the strong V-O bonds found for the larger clusters such as $V_4O_8^+$ may explain the difficulty of achieving oxygen transfer for larger clusters, rendering them inert towards CH_2F_2 , as observed experimentally. However, the cleavage of V-O bonds is not necessary in the reaction of $V_2O_4^+$ with CH_3CF_3 , and thus the reactivity of vanadium oxide cluster ions does not seem to depend on the cluster size for this reaction, again as observed experimentally.

Square-Wave (Magneto)Conductance through a Chain of Rings Due to Spin-Orbit Interaction

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We study ballistic electron transport through a finite chain of quantum circular rings in the presence of spin-orbit interaction (SOI) of strength a . The transmission and reflection coefficients for a single ring, obtained analytically, lead to the conductance for a chain of rings as a function of a and of the wave vector k of the incident electron. Due to destructive spin interferences the chain can be totally opaque for certain ranges of k the width of which depends on the value of a . A periodic modulation of a widens up the gaps considerably and produces a nearly binary conductance output.

Square-Wave, Spin-Dependent Transmission through Periodically Stubbed Electron Waveguides

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We study spin-dependent electron transmission T through waveguides (WGs) with periodically varied width c and strength α of the spin-orbit interaction. c is varied by attaching stubs to the WG, and α by applying gates. T can exhibit a nearly **square-wave** behavior as a function of the stub dimensions, of α , of the length of the gated subunit, and of the incident energy if only one mode propagates in the WG. If mode mixing is allowed the results become more complex but remain qualitatively the same. The transmission through a superlattice, with alternating segments of lengths l_1 , l_2 , and strengths α_1 , α_2 , is a periodic function of α_j and l_j , $j=1,2$. By simultaneously varying c and α one can very effectively control the gaps in the transmission, make them square and wide, block either spin state, and select the outgoing spin state.

Theoretical Investigation and Experimental Characterization of SMI Nanostructures

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This paper studies the physical properties of Self Assembled Ordered Polymer Structures. Previously, structures of water soluble nanotubes were made of SMA polymers; the polymer here is made from an SMI monomer and was studied to see whether it produced similar structures to SMA in solution. Molecular Modeling was performed using PM3 semi-empirical calculations and ab-initio, Hartree-Fock, calculations. Some of the calculations on SMI have been completed. The SMI polymer was not significantly soluble above pH 3, at which the concentration was of 0.5%. For low pH solutions, pH 1-2, the solubility increases to about 10%. AFM pictures were taken of SMI solution left to react with pyrrole. At pH 1, ring size nanostructures were obtained of ~50nm in diameter, which looked like donuts. At pH 3, AFM scans revealed the presence of long curved nanostructures of ~2000nm in length, shaped as paperclips.

Investigations into the Binding of an Organophosphorus Pesticide, Diazinon, with Cyclodextrins

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Organophosphorus pesticides are widely used for the control of unwanted plants and insects. As these synthetic compounds are released into the environment it is important that methods for their removal from contaminated sites be developed. Cyclodextrins (CDs) have the potential to bind to pesticide molecules and may in turn catalyze their degradation or increase their aqueous solubility such that they could be removed via a pump-and-treat method. The present study has used molecular dynamics (MM2) to model the binding of diazinon (1) with alpha-, beta- (2) and gamma-CD. Both binding depth and binding orientation were evaluated. Binding depth was the deepest with gamma-CD and shallowest with alpha-CD. The orientation of diazinon in alpha- and beta-CD was similar, with gamma-CD showing a different orientation. Modeling results have been instructive in the interpretation of studies by NMR and UV-VIS spectrophotometry to evaluate binding constants and the effect of CDs on the degradation of diazinon.

Surface Characterization and Catalytic Reactivity of Supported Bimetallic Molybdenum Oxide and Cerium Oxide for the Conversion of Heavy Crude Oils into Light Olefins and Transportation Fuels

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A series of silica-alumina supported molybdenum oxide, cerium oxide and cerium molybdate catalysts with varying amount of molybdenum oxide and/or cerium oxide has been examined by several surface characterization techniques. X-ray diffraction and Raman spectroscopy confirm the presence of cerium-molybdenum mixed oxide in the ceria promoted supported molybdena catalyst. The catalytic properties were evaluated for the selective deep catalytic cracking of n-hexane, used here as a model for petroleum naphthas. Cerium oxide, incorporated as a dopant in the supported cerium-molybdenum catalyst, has a main catalytic effect, which is to increase the selectivity to light olefins while the production of aromatics significantly decreases. However, when the ratio of [Ce]/[Mo] molar concentrations is higher than 0.8, the yield of product BTX (Benzene, toluene and xylene) aromatics rapidly increases at the expenses of that of light olefins. In addition to silica-alumina support, other oxidic supports were also examined. They include zirconia, γ -aluminum oxide and yttria stabilized alumina. The cerium oxide segregation effect was found to decrease in the order, γ -Al₂O₃ > SiAl > Y-Al > ZrO₂.

Nano-Structured Mesoporous Materials: Preparation and Characterization of Silica Nanoboxes

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Thermally and chemically resistant mesoporous materials were prepared by controlled dealumination of Na-X and Ca-A type zeolites using ammonium hexafluorosilicate method. The silica-richer parent zeolite, the smaller pore sized material produced and the narrower pore size distribution obtained. Temperature-programmed calcination of the dealuminated X-zeolite (ammonium form) resulted in (amorphous) silica nanoboxes exhibiting an ink-bottle shape, a quite high surface area (330 m²/g, no micropores), an average pore diameter of 4.5 nm with a quite narrow pore size distribution (± 1.0 nm) and finally, a pore opening diameter of 3.9 nm. The latter was determined by using the nitrogen sorption isotherms (BET technique) and related textural data. Incorporation of orthosilicate into the obtained mesoporous materials - called herein silica nanoboxes - in accordance with the recently developed technique for pore size engineering in zeolites, led to materials with smaller pore openings but having almost the same textural properties. Solid superacidic materials were prepared by incorporating a liquid superacid (triflic acid or trifluoromethanesulfonic acid) into the silica nanoboxes using various impregnation techniques. The maximum triflic acid loading which did not significantly affect the mesoporous framework of the materials was 10 wt %. As a reference, the maximum loading of less acidic sulfuric acid was much higher. Temperature-programmed desorption using a combined DTA/TGA system allowed the assessment of the amounts of the acidic species corresponding to the liquid and the bound phases, respectively.

A Quantum Chemistry Investigation of the Stability of $\text{Eu}^{3+}(\text{H}_2\text{O})_n$ Clusters with Respect to Deprotonation

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Despite intensive research over the last two decades, producing stable, multiply-charged, solvated metal ion clusters using traditional electro/laserspray techniques has proven to be a challenge to experimentalists. For instance, only a few studies have been devoted to the hydration of trivalent lanthanide ions in clusters and these clusters appear prone to dissociative electron or proton transfer, resulting in clusters of the form $\text{Ln}^{2+}\text{OH}(\text{H}_2\text{O})_{n-2}$ and the subsequent loss of the 3+ metal state. This is an intriguing finding of fundamental interest, given that the third ionization potentials of several Ln metals are lower than the second ionization potential of Cu, which is known to form stable divalent metal ion-water clusters, $\text{Cu}^{2+}(\text{H}_2\text{O})_n$. In this contribution, we present preliminary quantum chemistry calculations of the thermodynamics and possible mechanism of the deprotonation of $\text{Eu}^{3+}(\text{H}_2\text{O})_n$ clusters. Calculations reveal that the deprotonation of the cluster is thermodynamically very favourable even at relatively large cluster sizes, suggesting that $\text{Ln}^{3+}(\text{H}_2\text{O})_n$ clusters may not exist under most spray conditions and that theoretical studies of such model species may only serve to gain insight into the microsolvation of the trivalent metal ions in solution.¹

¹ Hughes *et al.*, *Int. J. Mass Spectrom.*, 241, 2005, 283-294.

Modeling the Conductance of Molecular Electronic Devices

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Molecular electronics poses a new challenge for quantum chemistry. In a typical molecular electronic device, a molecule is attached to two macroscopic metal contacts and the conductance $g(V)$ of the device is recorded as a function of the applied voltage (V). We develop theories that permit the calculation of $g(V)$. Various applications of our methods are presented that aim at understanding the electron transport through molecules. The systems studied include: gold wires, a cobaltocene based molecular quantum dot, a molecular photo switch, molecular diodes, etc.

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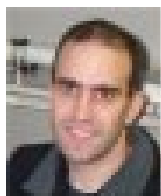
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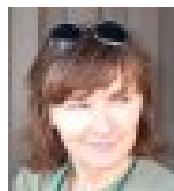
Physical Organic/
Macromolecular
Chemistry



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