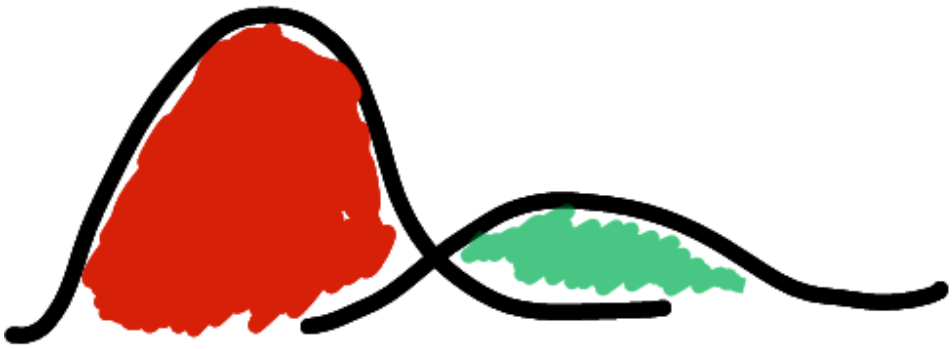
Proceedings



Theoretical Chemistry in Rio

Meeting to honor the 65th birthday of Prof. Marco Antonio Chaer Nascimento

June 11th and 12th, 2012

UFRRJ
UNIVERSIDADE FEDERAL RURAL DO RIO DE JANEIRO

Universidade Federal Fluminense

UFRJ
Universidade Federal do Rio de Janeiro

Scientific Program

June 11th – Monday

09:00-09:30	*Registration*
09:30-10:00	*Opening* (**Prof. Clarissa da Silva** - UFRRJ / **Prof. Pierre Esteves** - UFRJ)
10:00-10:30	*Presentation* - The academic and scientific trajectory of prof. Marco Antônio Chaer Nascimento **Prof. André Gustavo Barbosa** - *UFF (Brazil)*
10:30-11:30	Advances in the methods of quantum mechanics with applications to catalysis, materials science, fuel cells, and superconductivity. **Prof. William Goddard III** - *California Institute of Technology (USA)*
11:30-12:00	*Coffee break*
12:00-12:40	The impact of computational theory to heterogeneous catalysis: the mechanism of the Fischer-Tropsch reaction. **Prof. Rutger A. van Santen** - *Eindhoven Institute of Technology (Netherlands)*
12:40-13:20	Exciting world of theoretical studies of chemical reactions - from gas phase reactions to nano structures, catalysts, and enzymatic reactions. **Prof. Keiji Morokuma** - *Kyoto University (Japan)*
13:20-14:50	*Lunch*
15:00-15:40	Against NICS. **Prof. Paolo Lazzeretti** - *University of Modena (Italy)*
15:40-16:20	Multiradical systems the correct way: multireference calculations using COLUMBUS. **Prof. Hans Lischka** - *Texas Tech University (USA)*
16:20-16:50	*Coffee break*
16:50-18:00	*Poster Presentation*
19:00	*Social Dinner*

June 12th – Tuesday

09:30-10:00	Inner-shell electron energy loss spectroscopy and generalized oscillator strength at high momentum transfer. **Prof. Cassia Turci** - *UFRJ (Brazil)*
10:00-11:00	Solvents in Molecular Properties and Spectroscopy. Passive and Active Roles. **Prof. Sylvio Canuto** - *USP (Brazil)*
11:00-11:20	*Coffee break*
11:20-12:00	Towards the Development of a Molecular Mechanics Based Exclusively on Quantum Mechanics **Prof. Alfredo Simas** - *UFPE (Brazil)*
12:00-12:20	The molecular orbitals in density matrix functional theory. **Prof. Mario Piris** - *University of the Basque Country (Spain)*
12:20-12:40	Kinetic modeling of the competence between methyl and hydrogen scission of propane and the β-scission of the propyl radical using density funcional methods and chemical models **Prof. Oscar Ventura** - *Universidad de la República (Uruguay)*
12:40-14:10	*Lunch*
14:20-14:40	Molecular charge densities: fundamental aspects with applications to energetic materials and catalysis **Prof. Itamar Borges** - *IME (Brazil)*
14:40-15:20	Recent advances in computer-assisted probe discovery at LU/TBRRI. **Prof. Wely Floriano** - *Lakehead University (Canada)*
15:20-15:40	*Coffee break*
15:40-16:00	The trouble with benzene. **Prof. Thiago Cardozo** - *UFRJ (Brazil)*
16:00-16:30	How should the electronic structure look like to have an efficient organic solar cell? **Prof. Mario Barbatti** - *Max-Planck Institut (Germany)*
16:30-17:30	*Oficial Photo / Closing Ceremony* (**Prof. Claudio Costa Neto** - *UFRJ*)

Advances in the methods of quantum mechanics with applications to catalysis, materials science, fuel cells, and superconductivity

William A. Goddard, III

Charles and Mary Ferkel Professor of
Chemistry, Materials Science, and Applied Physics
Director, Materials and Process Simulation Center (MSC)
California Institute of Technology (139-74)
Pasadena, CA 91125

Advances in theoretical chemistry, computational chemistry, materials science, physics, and supercomputers are making it practical to consider first principles (de novo) predictions of important systems and processes in the Chemical, Biological, and Materials Sciences. Our approach is to build a hierarchy of models each based on the results of more fundamental methods but coarsened to make practical the consideration of much larger length and time scales. Connecting this multi-paradigm multi-scale hierarchy back to quantum mechanics enables the application of first principles to the coarse levels essential for practical simulations of complex systems.

We will highlight some recent advances in methodology such as:

- The ReaxFF reactive force field for predicting of reactive processes in large (millions of atoms) complex systems
- The eFF method for electron dynamics of (millions of electrons) highly excited complex systems
- PBE-lg and XYGJ-OS quantum mechanics methods for accurate intermolecular interactions
- The 2PT method for fast accurate calculations of entropy from molecular dynamics of large (50,000 atom) systems
- Then GEnSeMBLE Monte Carlo method for predicting 3D structures of GPCR membrane proteins
- The DarwinDock Monte Carlo method for predicting accurate ligand protein binding sites

Which we will illustrate with recent applications to Energy, Environment, Nanotechnology, Water, and Pharma selected from:

- fuel cell catalysts (oxygen reduction reaction) and electrolyte (alkaline)
- Photovoltaic (CIGS/CdS and dye synthesized systems)
- New materials for low pressure selective purification of water
- Organic cathodes for Li batteries
- Low energy electron enhanced etching in microelectronics processing
- DNA based self-assembly of Carbon nanotube arrays and devices
- Mechanism of superconductivity in cuprates strategies for increased Tc
- Materials for storage of H2, CO2, CH4
- Graphene electronics:
- Structure prediction of G-Protein Coupled Receptor Membrane Proteins (eg GLP1-R and CCR5)
- Design of new subtype selective ligands for control of HIV, obesity, Parkinson's, neo-natal meningitis

The impact of computational theory to heterogeneous catalysis: the mechanism of the Fischer-Tropsch reaction.

Rutger A. van Santen

Technical University Eindhoven

The performance of a catalyst is determined by its activity, selectivity and stability. In this lecture we will focus on selectivity. This determines atomic efficiency of the conversion of reagent to product.

The past decade has seen a paradigmatic change in catalysis science due to the spectacular new insights obtained due to advances in computational catalysis(1).

In order to use information on transition states to develop a predictive reactivity theory of catalysis, one needs to know or deduce the mechanism of a reaction. Current state of the art is such, that computations can be used to discriminate between different reaction mechanism(2). This can be used to a prediction of catalyst performance –structure and composition relationships, based on quantum-chemically computed data.

We will illustrate this approach by deducing such relationships for the Fischer-Tropsch reaction(3).This reaction is of current great practical interest because it converts synthesis gas into diesel. It is an important reaction step in the conversion of natural gas, coal or biomass into diesel.

Selectivity of heterogeneous catalytic reactions can appear under several different disguises:

- Composition and particle or cluster size of the reactive catalytic center.
- State of the catalyst surface
- Kinetics, especially for multifunctional catalysts

Kinetics plays an explicit role, when the overall reaction consists of consecutive reaction steps. The relative rates of the respective elementary reaction steps are essential, especially when in parallel non selective reactions may occur.

For transition metal catalysts overall performance may strongly depend on particle size, since different elementary steps may demand different structures of their reaction centers. The Fischer-Tropsch reaction, that converts synthesis gas into higher hydrocarbons has been shown to give only high selectivity when Co particles are not less than 6 nm. On the other hand smaller Ru particles at lower temperatures have increased selectivity for higher alcohols.

We will provide a unifying view of the chemistry that controls the different reactivity and selectivity aspects of the Fischer- Tropsch reaction supported by microkinetics simulations based on quantum-chemically obtained rate parameters.

1 R.A.van Santen, M.Neurock, Molecular Heterogeneous Catalysis, Wiley (2006)
2R.A. van Santen, M.Neurock,S.G.Shetty,Chem. Rev. 110,2005(2010)
3R.A. van Santen ,M.M.Ghouri,S.Shetty,E.J.M.Hensen, Catal.Sci. and Techn. 1,891(2011)

Exciting World of Theoretical Studies of Chemical Reactions – From Gas Phase Reactions to Nano Structures, Catalysts, and Enzymatic Reactions

Keiji Morokuma[1,2]

[1] *Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 606-8103, Japan*
[2] *Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, GA 30322, USA*

The chemical reaction which creates, destroys, reorganizes chemical bonds to produce new compounds is the most important subject of chemistry. I have been absorbed by this exciting world of chemical reactions from the beginning of my career for more than fifty years, since a hand-powered calculator was used to solve Hückel secular equations for frontier electron densities of simple aromatic hydrocarbons. Theoretical/computational studies have come a long way and are now playing the central role in understanding the mechanism and dynamics of chemical reactions and in helping designing more useful chemical reactions and catalysts. The theory can study not only the reaction of the ground state of molecules in gas phase but also reactions of excited electronic states as well complicated reactions of complex molecular systems. The information theoretical/computational studies can provide is often complementary to the information experimental studies provide, and research on chemical reactions is becoming impossible without strong collaboration between theorists and experimentalists.

I will discuss a few recent examples of our recent theoretical/computational studies on A. new paradigm in efficient determination of reaction pathways; B. self-assembly reactions of small carbon clusters to form fullerenes and carbon nanotubes; C. mechanism of photoactivatable molecular motor, D. reactions of metalloenzymes in protein environment, and E. chemical processes involving excited electronic states of biomolecules

Against NICS

Stefano Pelloni[a], Guglielmo Monaco[b], Riccardo Zanasi[b], and Paolo Lazzeretti[a]

[a] *Dipartimento di Chimica dell'Università degli Studi di Modena e Reggio Emilia via G. Campi 183, 41100 Modena, Italy email: stefano.pelloni@unimore.it, lazzeret@unimore.it*

[b] *Dipartimento di Chimica dell'Università degli Studi di Salerno via Ponte don Melillo, 84084 Fisciano (SA), Italy email: gmonaco@unisa.it, rzanasi@unisa.it*

A ring current model describing the flow of delocalized electrons, induced in unsaturated molecules by a magnetic field perpendicular to the molecular plane, has been developed to define simple and practical indices of current strength, which provide a reliable measure of aromaticity on the magnetic criterion. Comparison with corresponding *ab initio* estimates of current strength for a series of aromatic and antiaromatic systems is used to assess the quality of the proposed indices, which are shown to be preferable to others currently used, e.g., out-of-plane components of magnetizability, $\xi_{\parallel}$, and $NICS_{\parallel}$. It is also shown that these quantities are both biased by spurious geometrical parameters, which limit their practicality. In particular, $NICS_{\parallel}$ depends on the inverse of the ring radius and it does not provide acceptable magnetotropicity scales.

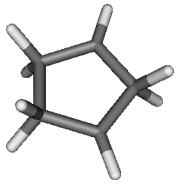
Keywords: magnetotropicity criteria, ring current models, magnetizability, nucleus-independent chemical shift, current susceptibility.
PACS: 33.15.-e; 33.15.Kr;82.56.-b

Multiradical systems the correct way: multireference calculations using COLUMBUS

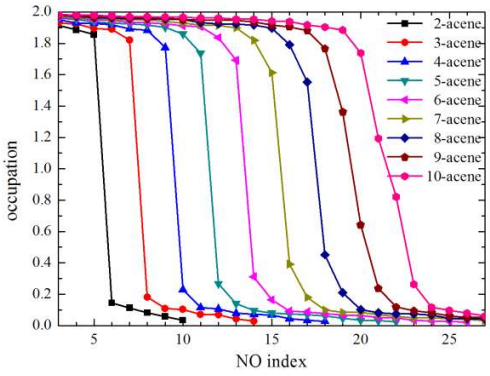
Hans Lischka

Texas Tech University
Lubbock, Texas
USA

The topic of this seminar are multireference calculations on interesting biradical and multiradical systems using the multiconfiguration self-consistent field (MCSCF), multireference configuration interaction (MRCI) and multireference averaged quadratic coupled cluster (MR-AQCC) methods available in the program system COLUMBUS. Two examples will be discussed. The first one is a biradical structure



derived from the thermal deazetization of a diazabicyclo[2.2.1]hept-2-ene, which leads to an interesting series of reactions and great challenges for interpretations. Secondly, the radical character of polyacenes and of graphene nanoflakes will be discussed. As an example, the figure below shows the evolution of the NO occupations with acene size and their increasing deviation from closed shell occupation.



Inner-shell electron energy loss spectroscopy and generalized oscillator strength at high momentum transfer

Cássia CuranTurci

Instituto de Química
Universidade Federal do Rio de Janeiro
Brazil

A general introduction to Electron Energy Loss Spectroscopy (EELS) and to Inner-Shell Electron Excitation is presented. Through the virtual photon model, an "Electrons versus Photons" comparison is made. The concept of Generalized Oscillator Strength (GOS) and its importance and a few practical applications sets the stage for this seminar.

Accurate information for representative species over the entire spectrum of energies is essential for the development and testing of new quantum mechanical procedures for calculating electronic state energies and the associated cross sections for the processes involved. Furthermore, adequate answers to questions about the effects of radiation can only be given if the associated cross sections are known. Such information not only permits a safer society, but also facilitates the development and use of radiation for worthwhile humanitarian purposes in a needy world.

Solvents in Molecular Properties and Spectroscopy. Passive and Active Roles.

Sylvio Canuto

Instituto de Física
Universidade de São Paulo

The accurate description of how solvent affects molecular properties and spectroscopy is crucial for understanding and rationalizing experimental studies. For this reason it is one of the central concerns in theoretical physical chemistry. In the last two decades great progress has been obtained by combining molecular mechanics and quantum mechanics (QM/MM). In this presentation we will briefly review some of our own developments and attempt to show interesting cases where the active role of the solvent is essential.

Towards the Development of a Molecular Mechanics Based Exclusively on Quantum Mechanics

Alfredo Mayall Simas

Departamento de Química Fundamental
Universidade Federal de Pernambuco
Recife, PE, Brazil

The foundations of a strategy to develop a molecular mechanics method based not on classical mechanics and force fields, but entirely on quantum mechanics and localized electron-pair orbitals, which we call quantum molecular mechanics (QMM), will be presented. The QMM procedure thus relies on the use of non-orthogonal doubly occupied spatial orbitals to describe the N-electron wave function of the system. These orbitals are pre-optimized in a form similar to the way the MM methods are parameterized, i.e., the method needs a set of parameters for each type of orbital (core, bonding or lone pair). QMM is thus non-iterative and requires only one extremely fast inversion of a single sparse matrix **T** to arrive to the one-particle density matrix, to the electron density, and consequently, to the *ab initio* electrostatic potential around the molecular system, or cluster of molecules, without ever needing to calculate the one- and two-electron integrals. Although QMM neglects the smaller polarization effects due to intermolecular interactions, it fully takes into consideration polarization effects due to the much stronger intra-molecular geometry distortions. Finally, we present the first practical applications of the QMM method by examining, in detail, the cases of clusters of helium atoms, hydrogen molecules, methane molecules, as well as the case of one molecule of HeH^+ surrounded by several methane molecules. For the case of methane, we show that QMM was able to reproduce satisfactorily the energetics and polarization effects of all distortions of the molecule along the nine normal modes of vibration, well beyond the harmonic region. We finally advance and discuss the potentialities of an exact formula to compute the QMM total energy, in which only two center integrals are involved, provided that the fully optimized electron-pair orbitals are known.

Reference

"Quantum molecular mechanics—a noniterative procedure for the fast *Ab Initio* calculation of closed shell systems",
G.L.C. Moura and A. M. Simas, J. Comp. Chem. 33 (9), 958-969 (2012). http://dx.doi.org/10.1002/jcc.22921

The Molecular Orbitals in Density Matrix Functional Theory

M. Piris[1,2], J. M. Matxain[1], X. Lopez[1], F. Ruipérez[1], J. Uranga[1],G. Merino[1,2], J. M. Mercero[1], J. M. Ugalde[1]

1 Euskal Herriko Unibertsitatea UPV/EHU and Donostia International Physics Center (DIPC), P.K. 1072, 20080 Donostia, Euskadi, Spain.
2 IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Euskadi, Spain
mario.piris@ehu.es

One-electron pictures have long helped to our understanding of chemical bonding. It has recently been pointed out [1] that density matrix functional theory (DMFT) can provide an orbital picture that agrees closely with the empirical valence shell electron pair repulsion theory (VSEPR) and the Bent's rule, along with popular theoretical methods like valence bond (VB) or linear combination of atomic orbitals - molecular orbital (LCAO-MO) methods.

The idea of a one-particle reduced density matrix (1-RDM) functional, or briefly density matrix functional, appeared few decades ago [2]. The major advantage of a density matrix formulation is that the kinetic energy is explicitly defined and it does not require the construction of a functional. The unknown functional only needs to incorporate electron correlation. The ensemble N-representability conditions that have to be imposed on variations of the 1-RDM are well-known. Here, the obstacle is the construction of the functional capable of describing a quantum-mechanical N-electron system. This functional N-representability is related to the N-representability problem of the two-particle reduced density matrix (2-RDM).

The 1-RDM functional is called natural orbital functional (NOF) [3] when it is based uponthe spectral expansion of the 1-RDM. An approximate NOF requires an expression of the 2-RDM in terms of the 1-RDM. Such reconstruction of the 2-RDM has been achieved using the cumulant expansion leading to the Piris NOF (PNOF) [4]. The PNOF is based on an explicit ansatz of the two-particle cumulant $\lambda(\Delta,\Pi)$ satisfying the D-, Q- and G-necessary positivity conditions for the 2-RDM. Appropriate forms of matrices $\Delta(\{np\})$ and $\Pi(\{np\})$ lead to different implementations PNOFi (i=1,5) [5].

In this presentation, the theory behind the PNOF5 is outlined. Some examples of strongly correlated systems, where density functionals yield pathological failures, are presented to illustrate the potentiality of the NOF theory. PNOF5 yields a remarkable accurate description of the homolitic dissociation of selected diatomic molecules. Compounds with full or partial diradical character have been also considered. In this talk, PNOF5 is applied to selected molecules that cover for ionic, polar covalent, covalent, multibonds (σ and π), 3c-2e and 3c-4e bonds. It will be shown that PNOF5 provides a localization scheme that yields an orbital picture in agreement with the chemical intuition.

The calculations were carried out with our implementation, the PNOFID code [6], based ona recent proposed algorithm [7] which yields the natural orbitals by an iterative

diagonalization of a generalized pseudo-Fockian matrix. Our results are accurate values as compared to high level wave function methods and available experimental data.

1. Matxain, J. M., Piris, M., Mercero, J. M., Lopez, X., Ugalde, J. M., *Chem. Phys. Lett.* (2012), DOI: 10.1016/j.cplett.2012.02.041; Matxain, J. M., et al., *ChemPhysChem.* (submitted).
2. Gilbert, T. L. *Phys. Rev. B*, 12 (1975) 2111-2120; Levy, M. *Proc. Natl. Acad. Sci. U.S.A.*, 76 (1979) 6062-6065; Valone, S. M. *J. Chem. Phys.*, 73 (1980) 1344-1349.
3. Piris, M. *Adv. Chem. Phys.*, 134 (2007) 387-427, and references therein.
4. Piris, M. *Int. J. Quantum Chem.*, 106 (2006) 1093.
5. Piris, M. *Int. J. Quantum Chem.*, (2012), DOI: 10.1002/qua.24020.
6. Piris, M. PNOFID, downloadable at http://www.ehu.es/mario.piris/#Software.
7. Piris, M., J. M. Ugalde, *J. Comp, Chem.*, **30**, 2078 (2009).

Kinetic modeling of the competence between methyl and hydrogen scission of propane and the β-scission of the propyl radical using density funcional methods and chemical models

Oscar N. Ventura

Computational Chemistry and Biochemistry Group (CCBG), DETEMA, Facultad de Química, UdelaR, CC1157, Montevideo, Uruguay

In this work we study the competence between the reactions of hydrogen and methyl scission during thermal cracking and combustion of propane, the emergence of the two isomers of the propyl radical, n-propyl and i-propyl, and their subsequent β-scission reaction to ethene and methyl radical. The purpose of the study was to analyze the accuracy of density functional methods as applied on this relatively well-known subset of the reactions implied in the production of propylene oxide from propane and propene. Conventional (B3LYP, B3PW91) and state of the art (PBE0, M06, BMK) DFT methods were employed, and their accuracy checked against experimental data and calculations done using model chemistries (complete basis set CBS-4M, QB3, and APNO, and G4 methods) and *ab initio* methods (MP2, CCSD(T) with a large 6-311++G(3df,2pd) basis set). The results obtained at the BMK level for the thermodynamics of the reactions are closer to experimental data than those afforded by any other DFT method, and very similar actually to CBS or CCSD(T) results, even if a medium size basis set is used. Activation energies are not however nearly as good, and root mean square errors of about 4 kcal/mol have been recorded. Ahrrenius parameters obtained using the BMK DFT method are semiquantitatively correct, when tunneling corrections are taken into account.

MOLECULAR CHARGE DENSITIES: FUNDAMENTAL ASPECTS WITH APPLICATIONS TO ENERGETIC MATERIALS AND CATALYSIS

Itamar Borges, Jr.

Dep. de Química
Instituto Militar de Engenharia
Rio de Janeiro, Brazil

The electron density or, the molecular charge density after inclusion of the positive nuclei contribution, is a key factor determining the behavior of molecules, thus of matter at the macroscopic level. Therefore, theoretical approaches to analyze it in a fundamental level are especially desirable. We present in this talk two general approaches to describe the molecular charge densities and related properties through chemically motivated partition techniques, illustrating them with recent applications to polynitroaromatics, components of explosives, and to molybdenum sulfide catalysts, largely used in the oil industry to remove sulfur contents.

References

- Silva, A. M., Borges Jr., I.; *How to find an optimum cluster size through topological site properties: MoS_x model clusters.* Journal of Computational Chemistry. , 32, 2186 - 2194, 2011.

- Moraes, T. F., Borges Jr., I.; *Nuclear Fukui functions and the deformed atoms in molecules representation of the electron density: Application to gas-Phase RDX (hexahydro-1,3,5-trinitro-1,3,5- triazine) electronic structure and decomposition.* International Journal of Quantum Chemistry, 111, 1444 - 1452, 2011.

- Anders, G., Borges Jr., I.; *Topological Analysis of the Molecular Charge Density and Impact Sensitivity Models of Energetic Molecules.* The Journal of Physical Chemistry A, 115, 9055-9068, 2011.

Recent advances in computer-assisted probe discovery at LU/TBRRI

Wely B. Floriano

Lakehead University (LU) and the Thunder Bay Regional Research Institute (TBRRI)

Imaging probes are compounds that target specific molecular processes associated to a disease or condition. There are two types of molecular imaging probes: (1) non-specific probes that are distributed or excreted by high capacity systems such as blood circulation, kidney, or liver, and are used to monitor blood flow, tissue permeability, or excretory processes, and (2) target-specific probes that bind to a molecular biomarker associated to a particular disease or condition. Presently, there is no systematic methodology that has been shown to be effective in the discovery of novel molecular probes. We combined computational and experimental approaches into a discovery platform to identify target-specific molecular probes suitable for fluorescence-based optical imaging or for Positron Emission Tomography (PET). We applied this research platform to two medically-relevant target proteins: the Human Papillomavirus 16 protein E6 (HPV16 E6), a proposed biomarker for cervical cancer, and Erythropoietin-producing hepatocellular carcinoma receptor B4 (EphB4), a receptor tyrosine kinase that has been implicated in cancer growth and metastasis. Chemical compounds with affinity for HPVE6 or EphB4 were identified by virtual ligand screening and tested experimentally for binding to the target protein in isolation and in a cell environment. The best positive compound tested against EphB4 is suitable for fluorescence labeling with amine-reactive dyes, and showed biological activity in both biochemical and cell based assays. The best positive compound tested against HPV 16 E6 is intrinsically fluorescent and also fluorinated, which makes it suitable for both optical and PET imaging and thus very desirable as molecular imaging probe. Additional probe candidates from the virtual ligand screening results are being used to construct a virtual library of near-infrared labelled compounds, which will be -rescreened against both targets. This secondary screening will allow the identification of probe candidates better suited for in-vivo imaging. These molecular probes will enable the development of novel detection assays and clinical tests, and the non-invasive monitoring of the efficacy of new drug candidates.

The trouble with Benzene

Thiago M. Cardozo

Instituto de Química
UFRJ

Understanding the nature of the chemical bonding in aromatic molecules is a challenge whose solution has eluded chemists for almost two centuries now. Even though partially working descriptions have existed for a long time, there is still much debate on the origin of the properties of molecules classified as aromatic.

In this work we present the failings of the more common explanations for this conundrum and some recent results which might point towards the correct description. These results were obtained by considering a separation of the electron density in its quasi-classical and quantum-mechanical parts, using the GPF-EP method [1]. The role of the pi electrons is re-evaluated and it is shown that the 6-electron bond concept advanced by Barbosa and Nascimento[2] is directly connected to the quantum-mechanical shaping of the electron density.

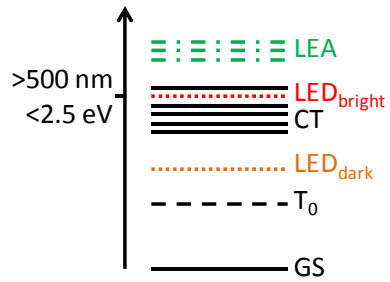
1 – Cardozo, T.M.; Nascimento, M.A.C. – *J. Chem. Phys.* **130**, 104102 (2009)
2 – Barbosa,A.G.H; "Mecânica Quântica de Muitas Partículas e a Teoria da Ligação Química", DoctorateThesis – Instituto de Química – Universidade Federal do Rio de Janeiro (2002)

How should the electronic structure look like to have an efficient organic solar cell?

Kakali Sen, Rachel Crespo Otero, Oliver Weingart, Mario Barbatti

Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1. D-45470 Mülheim an der Ruhr. Germany
barbatti@kofo.mpg.de tiny.cc/barbatti

In recent years, organic heterojunctions have been largely explored for photodevices. They are promising materials due to their potential low cost and plastic properties. The photophysics of an organic heterojunction composed of a donor and an acceptor is based on the photoexcitation of the donor, which is also a chromophore, followed by a charge transfer to the acceptor. For an efficient photodevice, this process occurs, ideally, with a very small charge recombination rate. Many groups around the world have proposed and tested a large number of different heterojunctions. In spite of all this effort, the efficiency of the organic solar cells is still very low in comparison to other classes of solar cells, barely reaching 10%. Even though the efficiency is set by several factors beyond the molecular level, especially the nanostructured distribution of donors and acceptors, it is desirable that the heterojunctions possess an electronic structure that maximizes the net charge separation. In this context, it is necessary to develop methods for simulation and for comparative evaluation of electronic properties of heterojunctions, which can be systematically applied to new designed heterojunctions, without the costs of the synthesis. We have proposed a series of criteria that the electronic structure of a heterojunctions should satisfy to maximize the exciton formation and minimize the charge recombination. These criteria are designed to allow a comparative evaluation of different heterojunctions. Qualitatively, they correspond to an electronic structure of the heterojunction whose charge transfer (CT) states and locally-excited (LE) states of the acceptor (A) and the donor (D) are distributed like in the diagram below. The approach is based on supramolecular quantum-chemical calculations of the electronic structure, followed by an automatic classification of the states based on their electronic density distributions. We have applied it systematically to investigate organic heterojunctions previously proposed in the literature composed of fullerene (acceptor) and several classes of donors (oligoacenes, oligothiophenes, triarylamines, oligo-para-phenylenes). We have also applied it to investigate newly designed donor units based on fused thiophene rings. These evaluation criteria and their application to a series of examples are discussed in this contribution.



Poster section

Index

Lithium Fluoride Nanotubes

Aline Verônica Henkes(PG) Marco Antonio Chaer Nascimento*(PQ).

Chemistry Institute, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil.
*email: chaer01@gmail.com

Key-words: lithium fluoride, nanotubes.

Nanostructured materials have shown unique physicochemical properties, which are quite different from those of the corresponding bulk crystals. Alkali halide materials, in particular lithium fluoride, are of special interest because of their stability and photoluminescence efficiency at room temperature.[1]

Recent calculations on a series of $(LiF)_{n=2,36}$ neutral clusters suggest that nanotube structures with hexagonal and octagonal transversal cross sections show stability equal to or greater than that of the typical cubic form of large LiF crystals.[2]

In order to further investigate such structures, accurate DFT and MP2 calculations have been performed on a series of $(LiF)_n$ (n up to 60) single-wall nanotubes, and the relative stability of $(MX)_{n=2,60}$ structural isomers was studied at the DFT (B3LYP/LAVCV3P**) level of calculation.

Figure 1 shows some examples of the isomeric forms investigated at the DFT (B3LYP/LAVCV3P) level of calculation. Both structures of Figure 1, the twin octogonal tubes $(LiF)_{48}$, and the honeycomb-like $(LiF)_{54}$ cluster, showed to be stable.

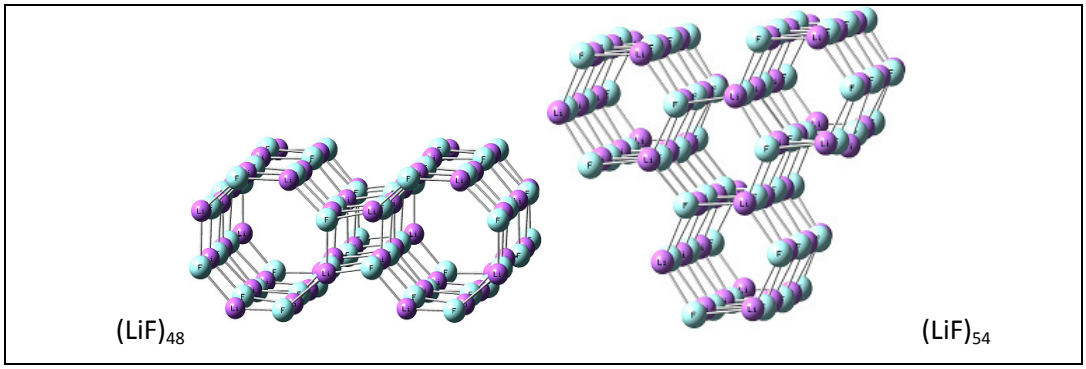


Figure 1. Condensed Nanotube structures.

These results suggest that a large variety of morphologies may exist for such materials and that these structures may find interesting applications in materials science.

Support: CNPq, CAPES, FAPERJ e INOMAT.

[1] Fernandez-Lima, F. A.; Ponciano, C. R.; da Silveira, E. F.;Nascimento, M. A. C. *Chem. Phys. Lett*. 2006, 426, 351.
[2] Fernandez-Lima,F. A; Henkes, A. V; da Silveira, E. F; Nascimento, M. A. C. *The Journal of Physical Chemistry C* 2012 *116* (8), 4965-4969.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

Atomic structure of Pt_n and Cu_n clusters: A density functional theory investigation

Anderson S. Chaves[1], Maurício J. Piotrowski[2], Juarez L. F. Da Silva[1,3]

[1] Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos

[2] Departamento de Física, Universidade Federal de Santa Maria, Santa Maria

[3] Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos

Key-words: Pt_n clusters, Cu_n clusters, DFT, atomic structures

The study of nanoclusters is increasingly expanding [1], which is mainly due to the great variety of possible technological applications, spreading from catalysis to magnetic storage and biomedical sensors. In particular, Pt-based clusters and nanoparticles have been widely studied due to the large number of applications of Pt in catalysis and electrochemistry, and hence, there is an increasing interest to obtain an atomistic understanding of the physical and chemical properties that play a role in the reactivity of clusters and nanoparticles. It is well known that our knowledge of the atomic structure of clusters and nanoparticles is a prerequisite to study the electronic properties and reactivity of clusters. However, due to the reduced dimensions of those clusters, experimental techniques have difficulties to access the atomic structure directly. In this work, we propose to use ab-initio calculations based on density functional theory within the generalized gradient approximation as implemented in the FHI-AIMS code [2] to study the atomic structure, electronic properties, and reactivity of Pt_n and Cu_n clusters (n = 2 – 15). We found that the effective coordination number of Cu clusters for n > 6 is close to the Lennard-Jones clusters, i.e., they form close packed clusters, which is expected as Cu crystallize in the face-centered cubic structure, however, the same is not the case for Pt clusters, which have much more open structures. For n = 3 – 6, the Cu_n clusters have two dimensional structures, which is similar to the structures reported for Al_n . In contrast with the bulk systems, which are non-magnetic, we found magnetic moments relative high for Pt_6 (8 μ_B) and Pt_8 (8 μ_B), however, Cu_n clusters have zero or 1 μ_B, which depends on the number of valence electrons in the structures. Furthermore, we will report results for the formation of PtCu cluster alloys.

[1] R. Ferrando *et. al.*, Chemical Reviews **108**, 845-910 (2008).

[2] V. Blum *et. al.*, Computer Physics Communications **180**, 2175-2196 (2009)

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

"Computational study of adsorption/ intercalation of hydrofluoric acid (HF) in hydrotalcites."

Anna Carolina de Azevedo Barbosa[1](IC), Deyse Gomes da Costa(PQ)[2], Viviane da Silva Vaiss(PQ)[1], Alexandre Amaral Leitão(PQ)[1]

[1]*Universidade Federal de Juiz de Fora. Instituto de Ciências Exatas – ICE. Departamento de Química. Rua José Lourenço Kelmer, s/n – Campus Universitário. Bairro Martelos CEP: 36036-900. Juiz de Fora – MG.*

[2]*Universidade Federal do Rio de Janeiro .Instituto de Física. Avenida Athos da Silveira Ramos, 149 - Centro de Tecnologia - Bloco A. Cidade Universitária - Ilha do Fundão. Caixa Postal: 68528 - CEP: 21941-972. Rio de Janeiro - RJ*

Key-words: hydrotaclites, fluoride, DFT calculations.

The layered double hydroxides (LDH) or hydrotalcite-like compounds, as they are usually known in the literature, are a class of compounds which can be represented by the following formula: $\left[M^{2+}_{1-x}M^{3+}_{x}(OH)_2\right]A^{m-}_{x/m}\cdot nH_2O$, where M^{2+} and M^{3+} are the divalent and trivalent cations, respectively; and A^{m-} is the interlayer anion. These compounds exhibit important properties, such as the anion exchange. The ion exchange capability allows their use as matrices for the immobilization of active species both for the remediation of wastewater, as for monitoring and seizing pollutants, for instance in the treatment of drinking water with high fluoride ions level. Although, the water defluoridation has been recognized in caries prevention, its excess can lead to serious problems like, dental and skeletal fluorosis. Due to the high efciency of the hydrotalcite-like compounds to remove anions from aqueous solutions, its versatility and simplicity, the use of LDHs as a fluoride absorbent has been gaining attention in recent years. By these reasons, the computational simulation is used to investigate the structure and features of layered double hydroxides and their reactions with anions like fluoride. In this present work, it was proposed the reaction between the hydrofluoric acid and the hydrotalcite with the formula: $\left[Mg_{14}Al_4(OH)_{36}\right]2CO_3\cdot 6H_2O$, and its reaction mechanism. The calculations performed are ab initio based on density functional theory with periodic boundary conditions. Plane waves were used as basis functions with an energy cutoff of 40Ry. Calculations were performed using the generalized gradient approximation for exchange and correlation corrections, and

pseudopotentials PBE (Perdew, Burke and. Erzenhof). The obtained results can help in some improvement of defluoridation technique. The mechanism consists of four elementary reactions. The first one, is based on the intercalation of the HF molecule between the layers. The second step represents the HF dissociation. On the next reaction occurs the donation of the H_2O molecule formed in the lamella for the interlayer space. At last, there is the desorption of this water molecule from the interlayer space. The thermodynamics was analyzed for the four reactions. It was observed that the free Gibbs energy was negative (-8.56 kJ/mol), indicating the spontaneity of the process, as well as the enthalpy (-8,87 kJ/mol), which means an exothermic process.

Support: CENPES, VALE.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

"Structural determination of mixed oxides of magnesium and aluminium by total energy calculation"

Carla Grijó Fonseca[1] (PG), Ary R. Ferreira[1] (PG), Sandra S. X. Chiaro[2] (PQ), Wladmir F. Souza[2] (PQ), Alexandre Amaral Leitão[1] (PQ)

[1]Department of Chemistry, Universidade Federal de Juiz de Fora – MG – Brazil.

[2]Petrobras-Cenpes, Ilha do Fundão, Rio de Janeiro - Brazil

Key-words: Mixed oxides, structural models.

Hydrotalcite-like compounds have been extensively used in the catalysis field in which they can act as catalyst, catalyst support or precursor for supports. The main reason for this is their ability to produce mixed metal oxide materials with a great surface area by thermal decomposition. Thus, the decomposition can be represented by:

$$Mg_{(1-x)}Al_x(OH)_2(CO_3)_{\frac{x}{2}}.mH_2O \rightarrow Mg_{(1-x)}Al_x\square_{\frac{x}{2}}O_{\left(1+\frac{x}{2}\right)}+\frac{x}{2}CO_2\uparrow+(m+1)H_2O\uparrow$$

Where □ is the vacancy.

In spite of the importance of the mixed oxides being recognized, the structure of these materials is not well-known. They are obtained in powder form and usually have low crystallinity degree, making it difficult to analyze in detail the structure of the mixed oxide by X-ray diffraction. RMN and EXAFS date showed that there is a migration of cations from the octahedral to tetrahedral sites during the decomposition process.

Previous efforts in order to obtain structural models for the mixed oxides by *ab initio* calculations were used as the basis for the implementation of a new route to search for better models for this compound, since this method does not cover all possible structures.

In this context, an extensive computational study has been performed in order to obtain structural models with different compositions that can simulate the structural characteristics of this compound. The relative stability between the different proposals will be evaluated via the total energy which will be initially calculated using interatomic potentials and then DFT calculations on promising cases. The models used in this study will be: MgO-type, Spinel-type and a non Spinel model.

Interatomic pair potentials are not as computationally expensive as quantum mechanics-based methods and allow the simulation of larger numbers of atoms. At first, tests were performed for the mixed oxides using parameterized Buckingham potential for the spinel ($MgAl_2O_4$). These tests showed promising results, however, we believe that the reparametrization of this potential can generate more accurate results.

We intend to achieve through an exhaustive analysis of possible models for the mixed oxide structures thermodynamically more favorable.

Support: Cenpes-Petrobras.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

"A discrete approach to the determination of protein structures using NMR data"

Virginia Costa (PG), Antonio Mucherino (PQ), Carlile Lavor (PQ), Luiz Mariano Carvalho (PQ), Nelson Maculan (PQ)

UFRJ, IRISA, UNICAMP,UERJ, UFRJ

Key-words: distance geometry, branch and prune, NMR experiments

We consider the problem of finding the three-dimensional conformation of a protein from a subset of inter-atomic distances provided by Nuclear Magnetic Resonance experiments [1]. The basic approach to this problem is to reformulate it as a continuous global optimization problem, where a penalty function is employed in order to measure the satisfaction of the constraints based on the known distances. Many methods have been proposed for the solution of this problem, and most of them are based on a search in a continuous space and/or on heuristic approaches to optimization. A recent survey on this topic can be found in [3]. We propose a discrete approach to this problem, where the search domain is reduced from a continuous to a discrete set which has the structure of a tree. Based on this combinatorial structure, we developed an efficient branch-and-prune (BP) algorithm [2]. Differently from the other algorithms, BP can enumerate all the possible mathematical solutions for a given instance, allowing to obtain multiple solutions to the problem. In this work, we explain how the discrete approach, previously applied just to protein backbones, can also be applied to the whole protein, including the side chains.

[1] G.M. Crippen and T.F. Havel, Distance Geometry and Molecular Conformation, John Wiley & Sons, New York, 1988.

[2] C. Lavor, L. Liberti, N. Maculan, A. Mucherino, Recent Advances on the Discretizable Molecular Distance Geometry Problem, European Journal of Operational Research 219, 698–706, 2012.

[3] L. Liberti, C. Lavor, A. Mucherino, N. Maculan, Molecular Distance Geometry Methods: from Continuous to Discrete, International Transactions in Operational Research 18, 33–51, 2010.

Support: FAPERJ, FAPESP, CAPES, CNPq.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

Transition energy and potential energy curves for ionized inner-shell states of CO, O_2 and N_2 calculated by several multiconfigurational approaches

Carlos E. V. de Moura (PG), Ricardo R. Oliveira (PG), Alexandre B. Rocha (PQ)

Grupo de Espectroscopia Teórica e Modelagem Molecular, IQ/UFRJ

Key-words: Inner-shell states, multiconfigurational method

Potential energy curves and inner-shell ionization energies of carbon monoxide, oxygen and nitrogen molecules are calculated by several forms of inner-shell multiconfigurational self-consistent field (IS-MCSCF) method, which is a protocol to obtain specifically converged inner-shell states at this level. The particular forms of this method are designated as IS-CASSCF and valence bond methods IS-GVB-PP and IS-SCVB. A comparison of these different versions of the IS-MCSCF method is carried out for the first time.

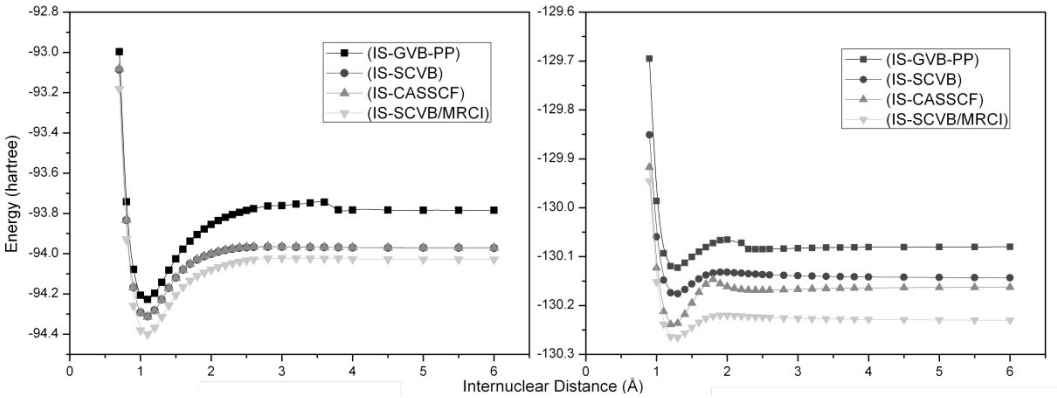


Figure 1. Potential curves for inner-shell ionized states. In the left, (N $1s^{-1}$) $^2\Sigma_u$ state in N_2. In the right, (O $1s^{-1}$) $^4\Sigma_u$ state in O_2. All calculations were done with Dunning's aug-cc-pVTZ basis set.

Molecule	GVBPP	SCVB	CASSCF	SCVB/MRCI	CASSCF/MRMP	Experimental
CO	295.91	295.38	295.38	295.59	295.73	296.13
N_2	403.38	402.94	402.95	402.98	410.35	409.90
O_2	532.46	532.04	532.35	531.41	544.35	543.37

Table 2. Inner-shell ionization energies calculated at several IS-MCSCF in electron volts (eV).

The SCVB/MRCI method did not succeed in improving the results coming from these multiconfigurational approaches. The best quantitative agreement can be obtained by using MRPT, in all variations of IS-MCSCF method.

Support: CNPq, FAPERJ.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

The search for a prototype of phospholipid membrane

Clarissa Oliveira da Silva[1](PQ), Cinthia Santos Soares[1](PG)

1. Universidade Federal Rural do Rio de Janeiro.

Keywords: conformation, phospholipids, phospholipid membrane

Trehalose dissaccharide allows the preservation of some biological materials under dehydration. One of the proposed mechanisms to that is the direct interaction between trehalose and the cell membranes of the biological material, where the disaccharide is assumed to replace water molecules after dehydration. The overall goal of our work is to obtain the values of interaction energy between trehalose, maltose and cellobiose and a prototype of phospholipid membrane. The simplest prototype proposed has two phospholipid (PHO) molecules.

Our prototype of phospholipid membrane comprises two molecules of dicaprilyl phosphatidylcholine (DCPC). Given the amphipathic nature of DCPC (Figure 1), we have chosen to study separately its polar (methyl-phosphocholine, MePC)[1] and apolar portions (dicaprilyl-ethyl, DCEt). The study of the polar fragment was already performed.[1]

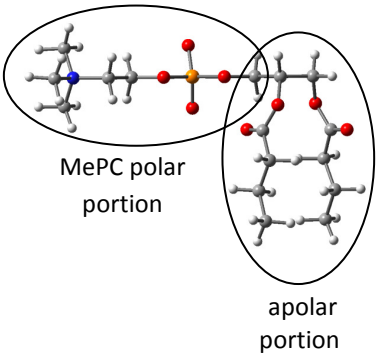


Figure 1 : polar and apolar units

The results in Table 1 refer to the apolar fragment (DCEt), and consists on the study of two different approximation modes of two different apolar units (parallel and perpendicular), reported in Figure 2, where the hydrogen atoms were omitted.

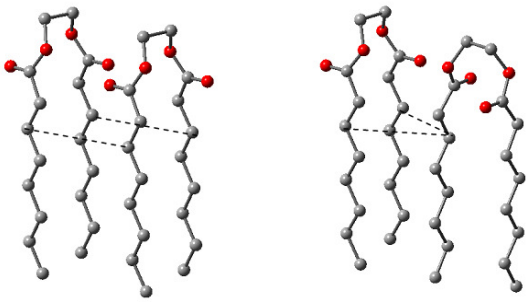


Figure 2 : Paralell and perpendicular approximations

All the calculations reported for DCEt units were performed in the gas phase and at B97-D/cc-p-DZV theory level.

In order to obtain how the stabilization energy between the nonpolar portions of two molecules of ($\Delta E_{stab}^{PHO\text{-}PHO}$) changes with the increasing of fatty acids carbon chains, the following procedure was performed: two previously optimized DCEt molecules were approximated, generating the dim8C system. This system had its geometry fully optimized. Four ~CH_2~ units were added to the optimized system, generating the dim9C system, which had their geometry fully optimized, and so on.

Table 1. $\Delta E_{stab}^{PHO\text{-}PHO}$ stabilization energy, in kcal/mol. The BSSE were not considered yet.

Dimer	$\Delta E_{stab}^{PHO\text{-}PHO}$ [1]	
	Paralell	Perpendicular
dim8C	-15,99	-13,95
dim9C	-18,83	-16,07
dim10C	-20,32	-17,48
dim11C	-22,95	-19,66
dim12C	-24,49	-20,91

According to the preliminary results, we conclude that the B97-D/cc-p-DZV theory level is suitable for the description of London forces between the apolar portions of membrane phospholipids. In the parallel approximation such forces are most intense that in the perpendicular one, being these values (after BSSE correction) assumed as the range in which the $\Delta E_{stab}^{PHO\text{-}PHO}$ due only to London forces, may vary.

Support: CNPq, FAPERJ.

[1] (a) Soares, C. S. and da Silva, C. O. Conformational study of methylphosphocholine: a prototype for phospholipidic headgroups of membranes. *Journal of Molecular Graphics and Modelling*, 2010, 29, 82-92. (b) Soares, C. S. and da Silva, C. O. Solvated potential energy surfaces for MePC. *Structural Chemistry*, 2011, 22, 885-891.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

"From simple oxides to complex biomaterials: when NMR calculations tackle experiments"

R. Lizárraga[1], E. Holmström[1], S. C. Parker[2], R. Auccaise[3], R. S. Sarthour[4], A. M. Rossi[4], C. Arrouvel[4]*

Institutional Addresses. [1] *Universidad Austral de Chile - Chile*

[2] *University of Bath -Bath - UK*

[3] *Empresa Brasileira de Pesquisa Agropecuária -Rio - Brasil*

[4] *CBPF, Rua Dr. Xavier Sigaud, 150 - Urca - Rio de Janeiro -RJ - CEP: 22290-180*

**Email: Corinne Arrouvel <c.arrouvel@bath.ac.uk>*

Key-words: density functional theory, chemical shift, ceramics

Elucidating the structure of complex solids can be theoretically and experimentally challenging. The properties of the ceramics can differ regarding different factors such as polymorphism, amorphisation, doping, size and morphology of particles. In the case of materials for medical applications, the experimental goal is to synthesize a stable bioceramic, resistant, biocompatible which favors the bone regeneration in the body fluid. While synthetic hydroxyapatite (HA) is one of the most promising candidates, its bulk and surface structures remain difficult to interpret especially when doped with cationic or anionic entities and when the presence precursors or side products is ubiquitous.

To achieve to a reliable description of the structure of complex ceramics, nuclear magnetic resonance (NMR) is an experimental technique often used to understand the local environment of ions in solids. The increase of the complexity of the systems tends to make the interpretation of NMR spectra harder. To make it possible, *ab initio* modeling using GIPAW method enables to bring new insight on the structural properties via the calculation of NMR chemical shifts and anisotropic parameters.

Through a DFT study of various crystalline and amorphous models of alumina, Lizárraga et al. [1] did resolve the uncertainty on structural parameters. For example, the authors claim that the best model of kappa-alumina is from the theoretical structure proposed by Smrcok et al. [2]. The Figure below is the simulated NMR spectrum of kappa-alumina in good agreement with available experimental NMR data.

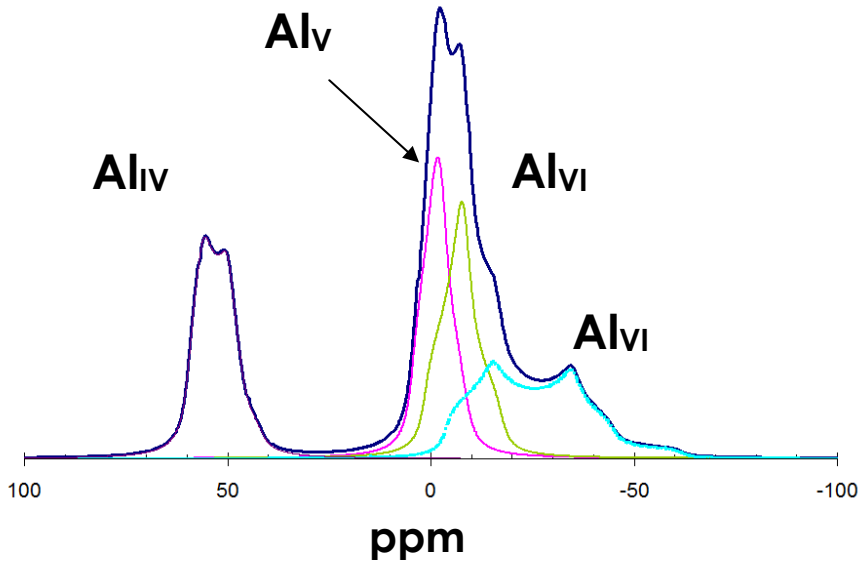


Figure: Simulated NMR spectrum of kappa-alumina from Smrcok *et al.*'s structure. (note: 0 ppm relative to Al_{VI} from calculated alpha-alumina)

The same method implemented in Quantum Espresso is being used to simulate doped HA, calcium phosphate and calcium silicate polymorphs. NMR being a quantitative and qualitative technique, a consistent comparison of simulated NMR spectra of various models combined with those obtained from experimental standard calcium phosphates aims to unpuzzle more complex structures of doped HA.

[1] R. Lizárraga, E. Holmström, S. C. Parker and C. Arrouvel, Phys. Rev. B, 83, 094201 (2011)
[2] L. Smrcok, V. Langer, and J. Krestan, Acta Crystallogr., Sect. C 62, I83 (2006).

Support: CNPq, CENAPAD.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

Describing thermochemical features of the HSeBr and SeBr molecules

Débora Barbosa Morf (IC), Willian Hermoso (PG), Fernando Rei Ornellas* (PQ)

Departamento de Química Fundamental, Instituto de Química
Universidade de São Paulo, São Paulo, SP, Brasil
**frornell@usp.br*

Keywords: Thermochemistry, CCSD(T), HSeBr

The importance of hypohalous acids in catalytic reactions of destruction of stratospheric ozone motivated our group to conduct a series of studies on isovalent compounds containing sulfur and selenium.[1-3] Expanding on this series of investigations, in this work we focus on a high-level theoretical determination of the energetic and thermochemical properties of the HSeBr and SeBr molecules. The computations were performed at the CCSD(T) level of theory using the aug-cc-pVnZ-PP (n = D, T, Q and 5) series of basis sets which include a pseudo-potential (PP) for the bromine and selenium atoms. The complete basis set (CBS) limit was estimated according to Feller *et al*.[4] Core-valence corrections were obtained with the CCSD(T)/cc-pwCVQZ-PP approach. Scalar relativistic corrections were performed using the Breit-Pauli Hamiltonian at the HF/aV5Z theory level. Molecular spin-orbit coupling corrections were estimated at the CASSCF/av5z level of theory, whereas the atomic coupling values were extracted from the literature.[5] Atomic heats of formation were obtained from the JANAF tables.[6] Total energies, zero-point energies, core-valence, spin-orbit coupling, and scalar relativistic contributions for the atomization energy and the heat of formation are shown below. With this new result, the calculated heats of formation at 298.15 K of the halogen series are predicted to be: 12.27 kcal/mol (HSeBr), 4.97 kcal/mol (HSeCl), and −22.81 kcal/mol (HSeF). For the enthalpy of the reaction HSeBr → H (^{2}S) + SeBr ($^2\Pi$), we obtained ΔH_r = 71.34 kcal/mol which can be compared with the values of 73.29 kcal/mol and 71.77 kcal/mol for HSeF and HSeCl, respectively. For SeBr, we predict ΔH_f (298.15 K) = 31.50 kcal/mol

Contribution	SeBr	HSeBr
E_{el} (CBS)[a]	-787.769547	-788.393689
ΔE_{el} [b]	56.70	134.58
E_{cv} [a]	-1.813372	-1.813936
ΔE_{cv} [b]	0.58	0.94
E_{sr} [a]	-0.673979	-0.674021
ΔE_{sr} [b]	0.10	0.12
E_{so} [b]	-2.78	0.00
ΔE_{so} [b]	-3.43	-6.21
ΔE_{zpe} [b]	-0.47	-4.97
ΣD_0 [b]	53.48	124.45
ΔH_f (0 K)[b]	32.60	13.26
ΔH_f (298.15 K)[b]	31.50	12.27

[a] hartree [b] kcal/mol

Our expectation is that this work can motive and guide future experimental studies on these compounds.

[1] Y.A. Aoto, F.R. Ornellas, *J. Phys. Chem. A* **2007**, 111, 521.
[2] W. Hermoso, F.R. Ornellas, *Chem. Phys. Lett.* **2009**, 479, 201.
[3] W. Hermoso, F.R. Ornellas, *Chem. Phys. Lett.* **2010**, 499, 213.
[4] D. Feller, K. A. Peterson, T. D. Crawford, *J. Chem. Phys.* **2006**, 124, 054107.
[5] A.A. Radzig, B.M. Smirnov, *Reference Data on Atoms, Molecules and Ions,* Springer-Verlag, Berlin **1985**.
[6] M.W. Chase Jr. *J. Phys. Chem. Ref. Data Monogr.* **1998**, 9, 1.

Support: FAPESP and CNPQ.

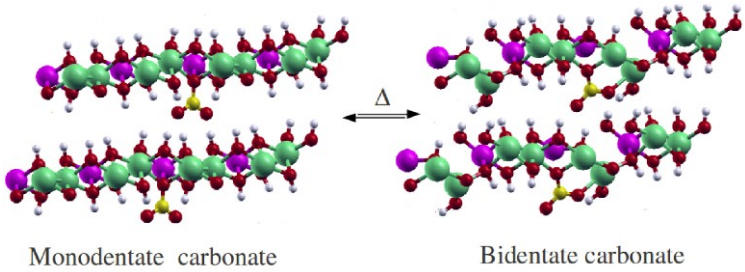
Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

Ab initio study of reaction pathways related to initial steps of thermal decomposition of the LDH compounds.

Deyse G. Costa[1](PG), Alexandre B. Rocha[2](PQ), Wladmir F. Souza[3](PQ), Sandra Shirley X. Chiaro[3](PQ), Alexandre A. Leitão[1](PQ)

1- Universidade Federal de Juiz de Fora (UFJF), 2-Universidade Federal do Rio de Janeiro (UFRJ), 3- PETROBRAS-CENPES

Key-words: Hydrotalcite, decomposition, monodentate and bidentate carbonate.



We present density-functional theory (DFT) calculations with periodic boundary conditions combined with thermodynamic and kinetic analyses to study the changes in the $[Mg_{2/3}Al_{1/3}(OH)_2](CO_3)_{1/6}.2/3H_2O$ LDH over a temperature interval equivalent to 25-350˚C. The inspection of five different hypotheses related to the decompositon reaction of this material suggest the mechanism: 1) The layered double hydroxide (LDH) contains H_2O molecules until 180˚C. 2) The next step involves the formation of a lamellar structure in which the CO_3^{2-} anions are incorporated to the layers as a monodentate ligand, at about 280˚C. 3) At 350˚C is observed a reorganization of the carbonate, which leads to a bidentate bond of this anion with the layer. So, the occurrence of two partially dehydroxylated intermeadiates containing a grafted carbonate was identified. The study of the grafting mechanism path also allows us to access structural information of all the intermediates and the transition structures along the reaction pathway, which can be divided into three parts: the vacancy formation, the incorporation of carbonate as a monodentate ligand and the CO_3^{2-} anion as a bidentate ligand.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

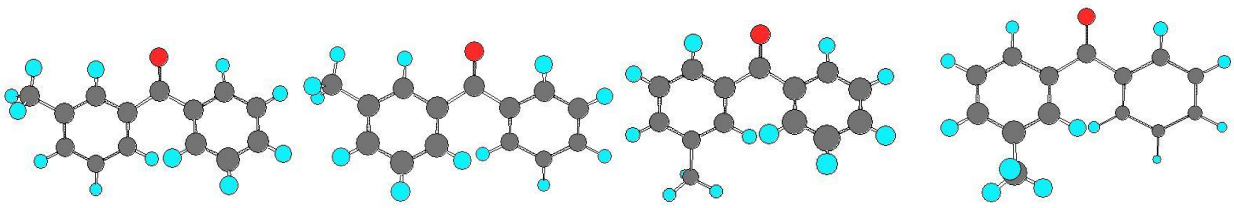
*C*onformational analysis of *m*-methylbenzophenone.

Diogo Monteiro Guimarães Ferreira (PG), Stella Maris Resende (PQ)

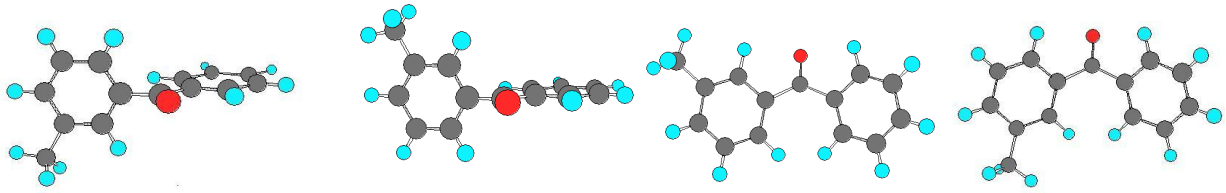
Laboratório de Química Atmosférica Teórica (LAQAT)
DCNAT, Universidade Federal de São João del-Rei, S.J.D.R., MG, Brasil.

Key-words: m-methylbenzophenone, conformational analysis, conformer, transition state, transition barrier.

Benzophenone and its derivates are used with numerous applications purposes. These ketones are used worldwide as sunscreens because of its high molar absortivity and mainly due to its capability of absorbing in, both, UVA and UVB simultaneously. A group substitution in benzophenone can lead to changes in the absortion. So, in this work, the goal is to proceed a conformational analysis of benzophenone's monosubstituted methyl derivative m-methylbenzophenone, in order to determine the most stable conformers. All calculations were conducted at the B3LYP/6-311G(3d,2p) level of theory, and stationary points characterization was done by means of harmonic frequencies analysis. The geometries of the four minimum energy conformers and the four transition states are presented below, along with the energies relative to the global minimum states (MIN1 and MIN2).



MIN1 | MIN2 | MIN3 ΔE= 0,17 kcal/mol | MIN4 ΔE= 0,17 kcal/mol



TS1 ΔE= 2,94 kcal/mol | TS2 ΔE= 2,94 kcal/mol | TS3 ΔE= 5,53 kcal/mol | TS4 ΔE= 5,78 kcal/mol

Support: UFSJ, CNPq, FAPEMIG.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

Theoretical Study of Aqueous Solvation Effect on the Geometric and Electronic Parameters of L-Ascorbic Acid Using Car-Parrinello Molecular Dynamics

Elisana Dias Barroso (PG), Ademir João Camargo (PQ), Solemar Silva Oliveira (PQ)

Unidade Universitária de Ciências Exatas e Tecnológicas (UnUCET), Universidade Estadual de Goiás (UEG)

Key-words: Molecular Dynamics, solvation

Ascorbic acid is a substance that has major applications in biochemical systems, pharmacology, electrochemistry and food processing. In this work we present a study of the L-ascorbic acid structure by Car-Parrinello molecular dynamics simulation. Furthermore, we observed the solvation process of the molecule of this substance in an aqueous environment with the aid of this method. This was arranged in a box containing water molecules. The systems were conducted to a minimum energy employing the steepest descent algorithms for the subsystem electronic and ionic subsystem for Damp. The simulation was performed using the Verlet algorithm for both subsystems. The results showed that the ascorbic acid molecule has a structure consistent with the results found by other methods and that the molecule in aqueous environment, is quite soluble in the regions of the-OH groups, however, slightly soluble in other regions of the molecule.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

"Density Functional Theory/GIAO/CSGT studies on (*E*)-2-Benzothiazole Hydrazones"

Eric B. Lindgren(PG)[1], Julliane D. Yoneda(PQ)[2], Katia Z. Leal(PQ)[1]

[1]*Instituto de Química, UFF, Niterói, 24020-141, Brazil*
[2]*Instituto de Ciências Exatas, UFF, Volta Redonda, 27213-415, Brazil*

Key-words: DFT, GIAO, CSGT, ^{1}H NMR, benzothiazole hydrazones

The antineoplastic activity of the benzothiazole nucleus is widely reported in literature. In a recent study, the in vitro anticancer activity of (*E*)-2-Benzothiazole hydrazones was evaluated. In this work, we present the comparison of the gauge-including atomic orbital (GIAO) and the continuous set of gauge transformation (CSGT) methods for calculating nuclear magnetic chemical shifts of seven (*E*)-2-Benzothiazole hydrazones at density functional theory (B3LYP and B3PW91) with cc-pVDZ basis set and integral equation formulation for the polarizable continuum model (IEFPCM).

In crystal state, these compounds are found to form symmetrical dimers, held by hydrogen bonds. The experimental NMR data suggests that dimers are also formed in solution, which would explain the highly deshielded hydrogens that would be involved in the hydrogen bonds. For the theoretical NMR calculations, the dimers were obtained by manual docking and its geometries were fully optimized using the B3LYP/cc-pVDZ and B3PW91/cc-pVDZ levels of theory (Figure 1). Since no imaginary frequency was found, the optimized structures were characterized as minima. All calculations were performed using the Gaussian 09W program.

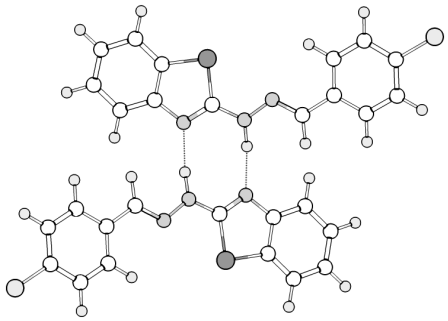


Figure 1: One of the (*E*)-2-Benzothiazole hydrazones dimers studied. Structure optimized by using B3PW91/cc-pVDZ level of theory

The best results were obtained at GIAO/B3PW91/cc-pVDZ level of theory, which showed the smallest root mean square errors and thus, can be used to calculate ^{1}H NMR chemical shifts with a high accuracy for (*E*)-2-Benzothiazole hydrazones.

Support: CAPES, FAPERJ

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

The role of polarization effects in geometric and thermodynamic properties of non-aromatic conjugated hydrocarbons

Felipe Fantuzzi(PG), Thiago M. Cardozo(PQ), Marco A. Chaer Nascimento(PQ)

Instituto de Química, Universidade Federal do Rio de Janeiro (UFRJ), Brasil

Key-words: interference effect, conjugated hydrocarbons

The nature of the chemical bond in non-aromatic conjugated hydrocarbon compounds is still the subject of theoretical investigations. Recently, the generalized product function energy partitioning (GPF-EP) method was developed, allowing the calculation of the quantum-mechanical interference and quasi-classical contributions of each chemical bond to the energy. Since interference is the main effect responsible for the formation of chemical bonds, the goal of this work is to apply the GPF-EP method to investigate the differences between the chemical bonding in conjugated and non-conjugated hydrocarbon isomers and to evaluate the contribution from the energy components to the stabilization of the molecules. It is shown that in all cases interference concentrates π electron density between the two carbon atoms directly involved in the (C-C)π bonds. For the conjugated isomers, this effect is accompanied by a considerable reduction of electron density in the π space of the neighbor (C-C)σ bond. On the other hand, quasi-classical effects are shown to be responsible for the extra stabilization of the conjugated isomers, in which a decrease of the π space kinetic reference energy seems to play an important role. Finally, it is shown that the polarization of p-like orbitals in compounds with alternating single and double bonds ultimately increases electron density in the π space of the neighbor (C-C)σ bond. Therefore, quasi-classical effects, instead of covalent ones, seem to be responsible for several properties of conjugated molecules, contradicting the usual attribution of stability due to bond delocalization.

Support: CAPES, CNPq, FAPERJ.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

"Determination of properties and structures of MoS2 and Co(Ni)MoS2 by *ab initio* calculations."

Florence P. Novais Antunes[1], Wladmir F. Souza[2], Sandra S. X. Chiaro[4] and Alexandre A. Leitão[1]

[1] *Departamento de Química, Universidade Federal de Juiz de for a (UFJF), Campus Universitário Bairro Martelos, 36036-330, Juiz Fora, MG, Brasil.*
[2]*PETROBRAS - Cenpes, Cidade Universitária, Ilha do Fundão, 21941-915, Rio de Janeiro, RJ, Brasil.*

Key-words: hydrodesulfurization, DFT calculation, MoS_2

Since the 50's, scientists have searched for catalysts to promote a more efficient removal of contaminants of fuels and, therefore, meet the increasingly demanding law regarding emissions from vehicles. A key component in this search involves the molybdenum disulfide, MoS_2, highly dispersed in the mass reaction environment in the form, or doped with nickel or cobalt, and anchored on the surface of inert carriers.

The process involves the removal of pollutants from the fuel in the presence of hydrogen. The MoS_2 belongs to a class of materials known as interlayer compounds, and it is in three polymorphic modifications. The most common phase (2H) occurs in nature in the form of molybdenum.

This system is very important and have many publications, but the mechanism of action of the disulfide molybdenum and the location of the dopant atoms, or also called promoters, were not clearly unveiled.

The sites of the surface are related to the catalytic activity and stability of the structure depends on the proportion of sulfur atoms on the surface. There are many publications showing the surface characterization, but many questions have not yet been answered, such as the adsorption of sulfur understanding and the nature of active sites, vacancy formation, the presence of promoters and their exact location, and the mechanism of subsequent hydrodesulfurization reaction.

The computer simulation has been assisting in the understanding of the structural properties and especially regarding the interaction with dopants and the thermodynamic analysis.

In this work, the cell structure of the bulk of MoS2 is reproduced and optimized under various parameters by *ab initio* calculations – DFT. Thereafter, the representation of the surface is obtained, built up from supercells 2x4x1, 3x4x1 and 4x4x1. The surface (10-10) is equivalent symmetry to the surface (100) being made by inserting a layer of vacuum in the crystallographic direction X, to generate the mentioned surface with the supercell.

Therewith, the influence of the proportion of sulfur and vacancies in the stability of different structures can be understood. It is also shown the study of surface of different ratios of promoter atoms of nickel and cobalt, and thereby, its best location and the proportion of the energetic point of view are defined. Having the stable surface in accordance with the proportion of sulfur and promoters, the study of the reaction dissociation of H_2 with the surface with and without the presence of promoter atoms.

Support: CENPES-PETROBRAS.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

A Product Branching Ratio Controlled by Vibrational Adiabaticity and Variational Effects: Kinetics of the H + *trans*-N_2H_2 Reactions

Jingjing Zheng[1] (PQ), Roberta J. Rocha[2] (PG), Marina Pelegrini[3] (PQ), Luiz F. A. Ferrão[2] (PG), Edson F. V. Carvalho[2] (PQ), Orlando Roberto-Neto[4] (PQ), Francisco B. C. Machado[2] (PQ), Donald G. Truhlar[1] (PQ)

[1]*Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota,USA;*
[2]*Departamento de Química, Instituto Tecnológico de Aeronáutica, São José dos Campos, SP, Brazil*
[3]*Divisão de Ensino, Academia da Força Aérea, Pirassununga, SP, Brazil*
[4]*Divisão de Aerotermodinâmica e Hipersônica, Instituto de Estudos Avançados, São José dos Campos, SP, Brazil*

Key-words: H+N2H2 reaction, Vibrational Effects, Branching Ration, ab initio

The abstraction and addition reactions of H + *trans*-N_2H_2 are studied by high-level ab initio methods and density functional theory. The reactants and transition states are optimized by CCSD(T) using the cc-pVTZ basis set and by the M08-SO density functional with two triple ζ basis sets, ma-TZVP and 6-311++G(2df,2p). Single-point point energies are also calculated by CCSD(T), CCSD(T)-F12a and CCSD(T)-F12b, and by various multireference methods (MRCI, MRCI+Q, MR-ACPF), and MR-AQCC) using CCD(T)/cc-pVTZ geometries. We calculated rate constants for these two reactions (**R1** H + *trans*-$N_2H_2 \rightarrow N_2H + H_2$ and **R2** H + *trans*-$N_2H_2 \rightarrow N_2H_3$) by multi-structural variational transition state theory with multidimensional tunneling and including torsional anharmonicity by the multistructural method. We find that the rate constant of the abstraction reaction has large variational effects, that is, the variational transition state yields a much smaller rate constant than the conventional transition state because it requires a much higher zero point vibrational energy. The addition reaction has a classical barrier height that is about 1 kcal/mol lower than that of the abstraction reaction, but the addition rates are less than the abstraction rates due to vibrational adiabaticity. The calculated branching ratio of abstraction to addition is 3.5 at 200 K and decreases to 1.2 at 1000 K and 1.04 at 2400 K.

Support: FAPESP, CNPq, U. S. Department of Energy

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

The role of interference energy in bond formation and conformational changes of saturated hydrocarbons

Francisco Senna[†] (PG), Thiago M. Cardozo (PQ), Marco A. Chaer Nascimento(PQ)

Instituto de Química, Universidade Federal do Rio de Janeiro (UFRJ), Brasil

Key-words: interference effect, saturated hydrocarbons.

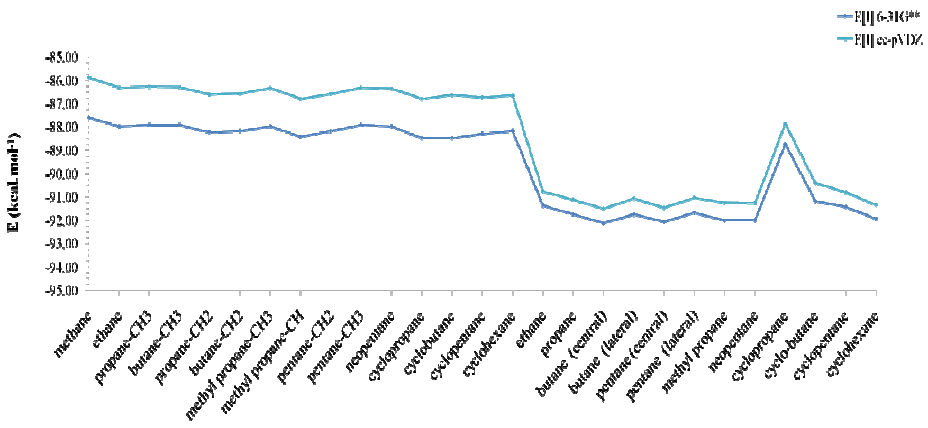
It is now well established that the driving force for the formation of covalent bonds is the quantum interference effect [1-4]. The changes in the electronic density, due to quantum interference, as the molecule is being formed, promotes a reduction of the kinetic energy and an increase of the potential energy in the internuclear region, in spite of the fact that the total kinetic energy increases while the total potential energy decreases as per the virial theorem. This fundamental mechanism of bond formation seems to be quite general as demonstrated in a series of papers [5-7] where the recently developed Generalized Product Function Energy Partitioning (GPF-EP) method [8] was applied to a variety of diatomic and polyatomic molecules.

There are, however, some important points which remain to be investigated. For example, how sensitive is the interference energy to the chemical environment of the pair of atoms involved in a chemical bond? Also, how is the strength of a chemical bond related to its interference energy? The answers to these and other related questions will be extremely important for establishing the transferability of the interference energy of a given bond to a similar one in a different molecule and to what degree can one estimate the bond energy based solely on the knowledge of its interference energy.

In order to try answering these questions we examined the interference energy in the C-C and C-H bonds of saturated hydrocarbons. This class of molecules is especially convenient to our purposes since it is experimentally known that most of the properties of those bonds are similar in all members of the series. All GPF groups corresponding to chemical bonds were calculated using GVB-PP (Perfect Pairing) wave functions to ensure the correct description of bond dissociations, and all core electrons were treated as single Hartree-Fock (HF) group. The results show that the main contribution to the formation of C–C and C–H bonds is the interference energy, as expected, although quasi-classical effects are mainly responsible for the energy differences due to chemical environment variations.

Support: CAPES, CNPq, FAPERJ.

[†]*Present address: Universidade Estadual de Campinas, Instituto de Química, Departamento de Química Analítica, Instituto de Química Cidade Universitária 13084-971 - Campinas, SP - Brasil - Caixa-Postal: 6154.*



Interference Energy

[1] Ruedenberg, K. *Rev. Mod. Phys.* **1962**, *34*, 326
[2] Wilson Jr., C.W.; Goddard III, W.A. *Chem. Phys. Lett.* **1970**, *5*, 45; *Theor. Chim. Acta* **1972**, *26*, 195
[3] Driessler, F. Kutzelnigg, W. *Theor. Chim. Acta* **1976**, *43*, 1
[4] Nascimento, M.A.C. *J. Braz. Chem. Soc.* **2008**, *19*, 245
[5] T. M. Cardozo and M. A. C. Nascimento. *J. Phys. Chem. A*, 2009, **113**, 12541
[6] T. M. Cardozo, G. N. Freitas and M. A. C. Nascimento. *J. Phys. Chem. A*, 2010, **114**, 8798.
[7]F. Fantuzzi, T. M. Cardozo and M. A. C. Nascimento. *Phys.Chem.Chem.Phys.* 2012, **14**, 5479
[8] T. M. Cardozo and M. A. C. Nascimento. *J. Chem. Phys.* 2009, **130**, 104102

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

"*In Silico* Study of the Catalytic Mechanism of Human Placental Alkaline Phosphatase"

Gabriela L. Borosky

Departamento de Matemática y Física, Facultad de Ciencias Químicas,

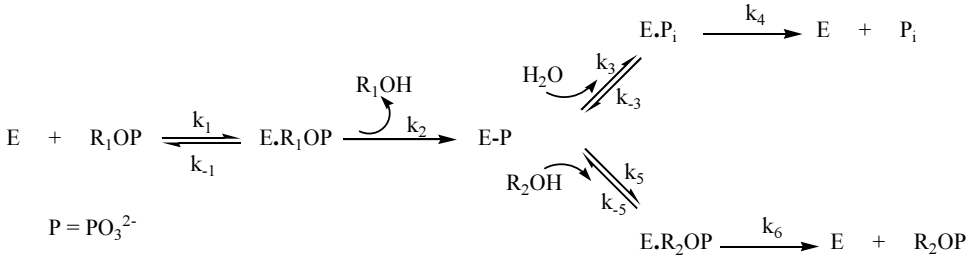
Universidad Nacional de Córdoba, INFIQC, CONICET, Ciudad Universitaria,

Córdoba, 5000, ARGENTINA. E-mail: gborosky@fcq.unc.edu.ar

Key-words: enzymatic activity, reaction mechanism, ONIOM calculations

Alkaline phosphatases (APs) are metalloenzymes found in many species from bacteria to man.[1] They catalyse the hydrolysis of phosphomonoesters with release of inorganic phosphate and alcohol.[2] The catalysis involves the activation of the catalytic serine, the formation of a covalent phosphoseryl intermediate, the hydrolysis of the phosphoseryl by an activated water molecule, and the release of the phosphate product or its transfer to a phosphate acceptor. Human placental AP (PLAP) is one of the four AP isozymes found in human.

In this work computational methods were applied with the aim of achieving a better understanding of the catalytic mechanism of PLAP. The active site of PLAP was modelled according to the crystal structure reported in the Protein Data Bank. The reaction steps of the catalytic mechanism were evaluated within the active site environment. Quantum-chemical calculations were performed employing the ONIOM procedure. In this way, DFT computations were carried out for the reacting phosphomonoester and catalytic serine, as well as for the metal cations, their ligands, and the water molecules involved in the catalytic mechanism, while a semiempirical hamiltonian was applied for the rest of the atoms. Free energies of activation ($\Delta G^{\neq}$) and of reaction (ΔG_r) were evaluated for each step of the mechanism of catalysis. Mechanistic variations according to the nature of the substrate (an aryl or alkyl phosphate) were examined.



1- McComb, R.B., Bowers, G.N. y Posen, S., en: *Alkaline Phosphatases* **1979**, Plenum Press: New York, pp 986-989.

2- Schwartz, J.H., Lipmann, F., *Proc. Natl. Acad. Sci. USA* **1961**, *47*, 1996-2005.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

Nanostructured Clay Minerals

Hélio A. Duarte[1], Luciana Guimarães[2], Maicon P. Lourenço[1], Maurício C. da Silva[1], Mateus P. Gouvea[1], Egon C. dos Santos[1]

[1]*Universidade Federal de Minas Gerais, Belo Horizonte-MG, 31.270-901, Brazil*
[2]*Universidade Federal de São João Del Rei, São João Del Rei, 36301-160, Brazil*

Key-words: SCC-DFTB, Imogolite, Halloysite, Chrysotile

The emerging field of nanotechnology is mostly focused on carbon and inorganic based nanomaterials, such as carbon nanotubes, graphene, transition metal nanotubes and nanowires. Naturally occurring clay minerals form also nanostructured layered materials and nanotubes with remarkable geometric properties. Since 2000, imogolite, halloysite and chrysotile gained prominence in the literature and appear as an emerging field of research, as it can be used as nanoreactors for selective catalysts, adsorbent, nanocable, support for the immobilization of metalloporphyrins, encapsulation, ion conductor and component in composites. The clay mineral nanotubes can be easily synthesized in mild conditions, functionalized and chemically modified[1,2]. Therefore, they are an important target for developing advanced materials[2,3].

Recently, imogolite, halloysite and chrysotile nanotubes have been investigated through Self Consistent Charge – Density Functional Tight Binding (SCC-DFTB) approximated method providing insights about their stability, electronic and mechanical properties of the clay mineral nanotubes[4,5]. Imogolite-like aluminogermanate nanotubes have been successfully synthesized[6]. We have shown recently from theoretical calculations that other imogolite-like structures can also be, in principle, synthesized.

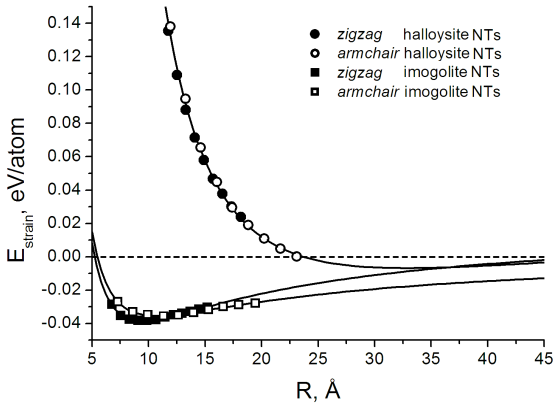


Figure 1: Strain energy as a function of tube radius for halloysite and imogolite nanotubes.

The results will be presented in the perspective of the nanomaterials development. Preliminary results about the functionalization and chemical modification of imogolite will be also presented.

Support: CAPES, CNPq, FAPEMIG, INCT-ACQUA

References

(1) Wang, L. J.; et. al.;. *Applied Surface Science* **2009**, *255*, 7542.
(2) Kang, D. Y.; *Acs Nano* **2010**, *4*, 4897.
(3) Kang, D. Y.; *Journal of Physical Chemistry C* **2011**, *115*, 7676.
(4) Guimaraes, L.; et al. *Acs Nano* **2007**, *1*, 362.
(5) Guimaraes, L.; et al. *J. of Phys. Chem. C* **2010**, *114*, 11358.
(6) Levard, C.; et al.; J. Am. Chem. Soc. **2008**, *130*, 5862.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

Conformational study of N-methylformamide dimers.

Honda, Diego E.(G), João B. L. Martins(PQ), José R.S. Politi(PQ)

Instituto de Química, Universidade de Brasília, CP 04478, 79910-900 Brasília, DF, Brazil

Key-words: N-methylformamide dimers, *ab initio*, rotational barrier

N-methylformamide is widely used as polar solvent in several applications of organic chemistry. The presence of O=C-NH moiety in its structure leads to a simple model for the peptide bonding, essential for the study of many biomolecules. The path to understanding its stabilization involves the understanding of weak hydrogen bonds, and these are of great importance for biological systems.

The aim of this work is to determine the barrier of rotation about the NC bond, to better understand their conformational preference, and to determine an analytical expression representing the rotation to be used in liquid computational simulation. To this end, we have performed *ab initio* electronic structure calculations, in each conformation determined by the angle of the CN bond. We have used the Hartree-Fock (HF) with 6-311G and aug-cc-PV5Z basis. These calculations were performed with the Gaussian 03 program. An extension of this study was performed using the G3 (Gaussian-3) composite method.

Preliminarily, analyzing the system in accordance to the atom electronegativities, it was expected that the cis-conformation was preferred. However, the trans conformation (Figure 1) is more stable of almost 25kJ/mol. As HF has known deficiencies for hydrogen bond treatment, work is underway to use correlated methods. Calculations are being performed at perturbation theory (MP2) and multiconfiguration (QCISD) levels. The results allow a deeper analysis of the interactions in this system, and making it possible to discuss the greater stability of the trans conformer.

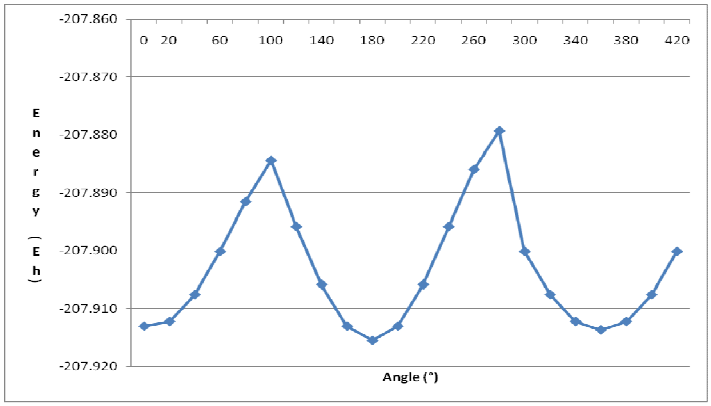


Figure 1 – Rotational Barrier: RHF/aug-cc-PV5Z (cis: 0° and trans: 180°)

Support: CNPq, Finatec, UnB

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

The connection between the upper and the lower energy regions of the potential energy surface of the ground electronic state of the HSO_2 system

Gabriel N. Freitas (PG)†, Juan D. Garrido (PQ)§, Maikel Y. Ballester (PQ)‡, Marco Antonio Chaer Nascimento (PQ)†

†Departamento de Físico-Química, Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, 21941-590, RJ, Brasil
§ Universidade Federal da Integração Latino – Americana, Foz do Iguaçu, 85867-970, PR, Brazil.
‡ Departamento de Física, ICE, Universidade Federal de Juiz de Fora, 36036-330, MG, Brazil.

Key-words: HSO_2, PES, Atmospheric Chemistry

The importance of the HSO_2 system in atmospheric and combustion chemistry has motivated several works dedicated to the study of associated structures and chemical reactions. Nevertheless, controversy still exists about a possible connection between the upper and lower-energy regions of the potential energy surface (PES) for the ground electronic state of the system. Very recently a path to connect these regions was proposed based on studies at the CASPT2/aug-cc-pV(T+d)Z level of calculation but the small energy difference between some of the transitions states along that path suggested the necessity of calculations at a higher level of theory. In the present work we report a CCSD(T)/aug-cc-pV(T+d)Z study of the stationary states associated to the proposed connection path, including assessment of the most reliable complete basis set (CBS) extrapolation scheme for the system. Among the new features, the present calculations show that there are no structures corresponding to the HSO_2(b) minimum and the TS3 saddle point obtained at the CASPT2 level and that the connection path between the upper and lower-energy regions of the PES for the ground electronic state involves only one transition state and most probably more than one electronic state.

Support: FAPERJ, CNPq.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

Vibrational relaxation vs reaction in OH + O_2 collisions under conditions of local thermodynamics disequilibrium.

Diana Rodríguez Linares (PG)†, Pedro H. A. Konzen (PQ)§, Juan D. Garrido (PQ)§

†*Departamento de Físico-Química, Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, 21941-590, RJ, Brasil*
§ *Universidade Federal da Integração Latino – Americana, Foz do Iguaçu, 85867-970, PR, Brazil.*

Key-words: Ozone, Chemical Kinetics, Atmospheric Chemistry, Ozone Deficit Problem

The vibrational relaxation processes occurring during collisions of vibrationally excited O_2 and OH are investigated using the quasiclassical trajectory method and a double many-body expansion (DMB I) potential energy surface for ground electronic state HO_3.
A model is presented to compare the reactive and vibrational relaxation processes occurring in collisions of vibrationally excited O_2 and OH. A steady-state approach is then used to evaluate the master equations leading to production of “odd-oxygen”. A comparison with the traditional Chapman rate and the Wodtke mechanism for ozone formation is also presented. It is shown that vibrational relaxation does not eliminate the possibility of reactive collisions leading to “odd-oxygen” formation at sufficiently high altitudes and hence ozone formation under stratospheric and mesospheric local thermodynamic disequilibrium (LTD) conditions can be effective. The calculated values for the additional “odd-oxygen” production may account for the reported ozone deficit in the tropics.

Support: CAPES, CNPq.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

"On the nature of inhibition performance of imidazole on iron surface."

Juliana Mendes (PG), Edilson Clemente da Silva (PQ) and Alexandre Rocha (PQ)

Universidade Federal do Rio de Janeiro, Instituto de Química, CEP 21941-909, Rio de Janeiro, Brasil.

Key-words: Adsorption, iron surface, imidazole.

Although spontaneous, corrosion is commonly an undesirable process that should be controlled. Find ways to manage the process of corrosion is of great importance for the oil industry. One feasible way to control corrosion is through the use of corrosion inhibitors, which are substances that offer protection to the metal surface by making chemical bonds with it. It is well known that organic molecules containing electron donor atoms like nitrogen, oxygen or sulfur, act as corrosion inhibitors. Imidazole is one of such molecules. Its structure is described as an organic heterocycle containing two nitrogen atoms, one of them being of pyrrol and the other being of pyridine type.

The aim of this work is to study the adsorption of imidazole on the iron surface to better understand the mechanism of protection by a corrosion inhibitor in a metallic surface.

The methodology used in this work is the density functional theory using the PBE exchange-correlation functional, combined with periodic boundary conditions, plane waves basis set (Bloch's theorem) and pseudopotentials.

Initially, we have studied the preferred site of adsorption of a single imidazole molecule on the (001) iron surface. The imidazole bonded by nitrogen lone pair and having the ring plane perpendicular to the iron surface provided the lowest energy when localized on the top site of the surface. The case where imidazole is bound by the imidazolic ring - parallel position - provided the lowest energy when localized in the hollow site. The former is the most stable in absolute terms. The study was then extended to the adsorption of several molecules in order to describe the passivation film. It was found that there exists a cooperative interaction of adsorbed imidazole molecules.

Support: FAPERJ, CNPq and CAPES.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

"Are Different L_4 ligands able to affect the Ru-NO and Ru-NO_2 bonding situation in Ruthenium Nitrosyl Complexes?"

Karla F. Andriani (PG),[1] Fabio G. Doro(PQ),[2] Giovanni F. Caramori(PQ)[1]
[1]Departamento de Química, 88040-900, Universidade Federal de Santa Catarina - UFSC, Florianópolis, Santa Catarina, Brasil.
[2]Departamento de Química Geral e Inorgânica, Instituto de Química, 40170-290, Universidade Federal da Bahia – UFBA, Salvador, Bahia, Brasil.

Key-words: LMO-EDA, QTAIM, ELF, NBO

Nitrosyl ruthenium complexes have been received considerable attention due to the ruthenium affinity for NO and its abilities to store, transfer and release NO in many biochemical processes occurring on different cells and tissues[1]. The use of ammines and polyamines as ligands allow a more NO controlled release, since as expected that cyclic polyamines promote an increase on stability than non-cyclic polyamines[2]. Ruthenium nitrosyl complexes such as *cis*-$[Ru^{II}(NO)(NO_2)(NH_3)_4]^{2+}$ (**1**), *cis*-$[Ru^{II}(NO)(NO_2)(bipy)_2]^{2+}$ (**2**), and *cis*-$[Ru^{II}(NO)(NO_2)(phen)_2]^{2+}$ (**3**), at ground and metastable states were investigated at the light of the energy decomposition analysis (LMO-EDA) at DFT level (M06/Def2-SVP,Def2-TZVP). Additional insight about the Ru-NO and Ru-NO_2 bonding situation was also provided by using QTAIM, ELF, and NBO analyses.

The LMO-EDA results suggest that the magnitude of Ru-NO and Ru-NO_2 interactions in complexes **1**, **2** and **3** is modulated by polarization and electrostatic terms, respectively. The polarization term for Ru-NO interaction is larger in complex **1** than in **2** and **3**, when cyclic ligands are present. However the electrostatic term for Ru-NO_2 bond presents the opposite behavior, it is smaller in **1** than in **2** and **3.**

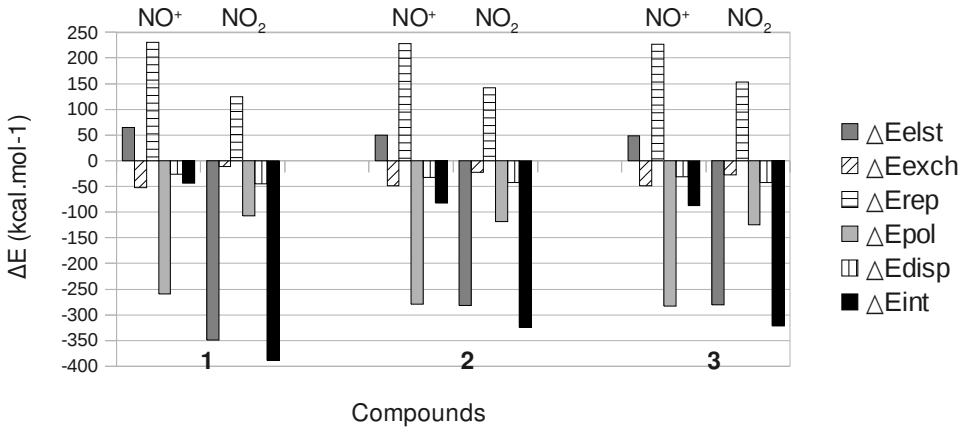


Figure 1 – LMO-EDA analysis of cis-$[Ru^{II}(NO)(NO_2)(NH_3)_4]^{2+}$ (**1**), cis-$[Ru^{II}(NO)(NO_2)(bipy)_2]^{2+}$ (**2**), cis-$[Ru^{II}(NO)(NO_2)(phen)_2]^{2+}$ (**3**), where the terms are depicted as following, ΔE^{elst}=electrostatic energy, ΔE^{exch}=exchange energy, ΔE^{rep}=repulsion energy, ΔE^{pol}=polarization energy, ΔE^{disp}=dispersion energy, ΔE^{int}=total energy.

[1] F. G. Marcondes et al. *Life Sciences 70*, **(2002),** 2735–2752.
[2] C. R. Pestana et al. *Nitric Oxide 20*, **(2009)**, 24–30.

Support:FAPESC/CNPq (Grant. 17.413.2009-0)

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

"A General Program for Constructing Specific Force Fields"

Laura Lopes (PG), Marco A. Chaer Nascimento (PQ)

Instituto de Química, Universidade Federal do Rio de Janeiro

Key-words: Force Field

Classical simulations are often made with standard generic force fields, provided by both commercial and freely distributed packages. However, several materials studied nowadays require specific force fields to describe them, taking into account important interactions for the process to be simulated.

The goal of this work is to develop a general program to construct specific force fields. The force field expression is chosen by the user among an extensive database to represent each of the bonded and non-bonded terms. The fit of the parameters is performed either with the Levenberg-Marquardt Method (a least squares method)[1] or using the *hessian biased method* [2] . In the first case, the force field parameters are optimized to reproduced data obtained by *ab initio* calculations, while in the second case the force filed parameters are obtained by forcing the force field hessian matrix to reproduce the experimental vibration frequencies.

In order to test the program, several force fields available in the literature were reproduced. In addition, force fields to represent metallic clusters are being developed. The program is written in FORTRAN 95 language.

Support: CNPq, FAPERJ, Instituto Nacional de Materiais Complexos Funcionais (INOMAT)

[1] Numerical Recipes in Fortran 77 : The Art of Scientific Computing, Cambridge University Press, 1986-1992

[2] Siddharth Dasgupta and William A. Goddard III , J. Chem. Phys. 90, 7207 (1989)

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

"Effect of CO2 concentration on the local enviroment structure of ionic liquid 1-ethyl-3-methylimidazolium bis(trifluorosulphonyl imide) - emim[Tf2N]"

Luciano T. Costa (PQ), David van der Spoel (PQ), Giane B. Damas (PG) e Tuanan da Costa Lourenço (G)

Universidade Federal de Alfenas, rua Gabriel Monteiro da Silva 700 Alfenas-MG

CEP 37130-000

Key-words: ionic liquids, molecular dynamics, carbon dioxide, clean technology.

The carbon dioxide emission on the atmosphere is an emergent problem of the humanity. Recent review shows that the available conventional tools is not efficient to remove greenhouse gases such as CO_2 and that the new solutions are being proposed in order to substitute it. This possibility opens a new research topic and becomes a challenging in CO_2 capture, in which ionic liquids have been applied.

This work aims to study the effect of CO_2 concentration on the local environment structure of 1-ethyl-3-methylimidazolium bis(trifluorosulphonylimide), emim[Tf2N], by molecular dynamics (MD) simulations and quantum chemistry calculations. We have performed MD simulations of the neat ionic liquid and also of the emim[Tf2N]/CO2 systems, in which the amount of CO_2 into the ionic liquid was: 20, 50, 83. 173, 204 molecules. It was used 160 ion pairs in each system.

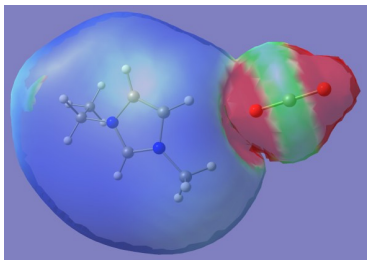


Figure 1. Electrostatic potential for the cation-CO2 interaction obtained from B3LYP/6-311G(d,p) level of theory of the equilibrium structure derived from MD simulations.

Radial distribution functions were calculated for cation-anion, cation-cation and anion-anion interactions for neat ionic liquid and also for systems containinig CO_2. Results reveal that the equilibrium structure of IL is not modified, even when the CO_2 molecules are located into the empty spaces between ions. Local environment structure have been investigated using ab initio calculations (see Fig 1.) on the equilibrium structures derived from MD simulations.

Support: **FAPEMIG**

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

One-Electron Properties Calculations of *AH* Molecules using *MRHFCI* Method

Luiz Augusto Carvalho Malbouisson[1] (PQ), Antonio Moreira de Cerqueira Sobrinho[1] (PQ), Micael Dias de Andrade[1] (PQ)

[1]*Instituto de Física da UFBa*

Key-words: Multiple Hartree-Fock Solutions, Multi-Reference CI, Quadrupole Moment

In previous works [1, 2], we have introduced a new multi-reference configuration interaction method based on multiple Hartree-Fock (HF) solutions (named as MRHFCI). In this method, instead of using a single reference – the HF fundamental state – we apply several HF extremes as references to expand the state functions. In order to perform the MRHFCI calculations, it is necessary to determine multiple HF solutions with the appropriate symmetries of point and spin. Using the MRHFCI with the STO-6G, CFG-6G [3], DZ, TZ and DZp atomic bases, we have obtained, for some AH molecules (A – first row element), values of the permanent electric dipole moment for the above systems and bases quite close to the experimental values with a reduced number of configurations in the MRHF bases.
In recent work [4], using the MRHFCI with the STO-6G and CFG-6G bases, we have found the electrical dipole and quadrupole moment values for the Hydrogen Fluoride molecule, close to the experimental values. In this work we calculate with the MRHFCI method the quadrupole and the polarizability for this and other AH systems.

[1] MALBOUISSON, L. A. C.; MARTINS, M. G. R. and MAKIUCHI, N.; Int. Journal of Quantum Chemistry, 106 (2006) 2772;
[2] SOBRINHO, A. M. C.; NASCIMENTO, M. A. C.; de ANDRADE, M. D. and MALBOUISSON, L. A. C.; Int. Journal of Quantum Chemistry, 108 (2008) 2595;
[3] de ANDRADE, M. D.; NASCIMENTO, M. A. C.; MUNDIM, K. C.; SOBRINHO, A. M. C. and MALBOUISSON, L. A. C.; Int. Journal of Quantum Chemistry, 108 (2008) 2486;
[4] MALBOUISSON, L. A. C.; de ANDRADE, M. D. and SOBRINHO, A. M. C.; Submitted for publication in the Int. Journal of Quantum Chemistry.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

"Electronic and geometrical properties of $CFCl_3$ in vacuum and in aqueous solution, using Car-Parrinello molecular dynamics"

Mary Hellen da Costa Monteiro(PQ), Ademir João Camargo (PQ),
Solemar Silva Oliveira(PQ)

Unidade Universitária de Ciências Exatas e Tecnológicas (UNUCET)
Universidade Estadual de Goiás.

Key-words: Molecular Dynamics, $CFCl_3$ and Car-Parrinello.

We have studied the $CFCl_3$ (Freon-11) hydration process. For this study, the molecule of $CFCl_3$ was initially simulated in vacuo using the molecular dynamics algorithm of Car-Parrinello, where the structural parameters were obtained. Subsequently, the molecule was prepared in a box containing 18 water molecules, where the new system was evaluated by simulation using the same algorithm. The minimization of both systems was performed with the aid of the steepest descent algorithm and Damp. The molecular dynamics simulation was performed with the aid of the Verlet algorithm. The wave functions were expanded on a basis set of plane waves, using the Vanderbilt pseudopotentials to describe the ionic core electrons. The temperature of molecular systems studied was kept constant at a value of 300 K by using the thermostats Nosé-Hoover.

It was observed from this study that $CFCl_3$ molecule, although very polar, does not interact with water molecules, presenting an hydrophobic tendence.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

"Interactions between $[BMIM]^+[BF4]^-$ and γ-Al_2O_3 (100) surface calculated by DFT"

Mateus J. F. Martins[1], Ary R. Ferreira[1], Elena Konstantinova[2], Heitor A. de Abreu[3], Wladmir F. Souza[4], Sandra S. X. Chiaro[4], Luís G. Dias[5] and Alexandre A. Leitão[1]

[1]Departamento de Química, Universidade Federal de Juiz de Fora (UFJF), Campus Universitário Bairro Martelos, 36036-330 , Juiz de Fora, MG, Brasil.

[2]Departamento de Educação e Ciências, IFSudeste MG (IFET), Campus Juiz de Fora, 36080-001, Juiz de Fora, MG, Brasil.

[3]Grupo de Pesquisa em Química Inorgânica Teórica, Departamento de Química, ICEx, Universidade Federal de Minas Gerais (UFMG), 31270-901, Belo Horizonte, MG, Brasil.

[4]PETROBRAS - Cenpes, Cidade Universitária, Ilha do Fundão, 21941-915, Rio de Janeiro, RJ, Brasil.

[5]Departamento de Química , Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto (FFCLRP), Universidade de São Paulo (USP), Campus da USP, 14040-901, Ribeirão Preto, SP, Brasil.

Key-words: γ-Al_2O_3; ionic liquids; adsorption simulation; DFT calculations; dispersion forces; catalyst support.

The main aim of this work is to investigate the 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF4]) ionic liquid (IL) adsorption on the γ-Al_2O_3 (100) by density functional theory (DFT) calculations to try to rationalize the adsorption as an eletrostatic phenomenon. Optimized geometries and interaction energies of the ionic liquid on the γ-Al_2O_3 were obtained on high surface coverage (one cation-anion pair per 94.96 nm^2). A study of dispersion force was made to estimate its contribution to the adsorption. Overall, the process is ruled by electrostatic interaction between ions and surface. Adsorption of the anion $[BF4]^-$ and cation $[BMIM]^+$ were also studied by Bader charge analysis and charge density difference for supported and unsupported situations. It is suggested that the IL ions have their

charges maintained with significant anion cloud polarization inward to the acid aluminum sites.

Support: CENPES-PETROBRAS.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

Transition-metal clusters encapsulated into fullerenes: A density functional investigation

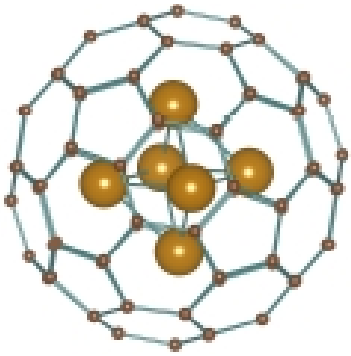
Polina Tereshchuk [1] and Juarez L. F. Da Silva [1,2]

University of São Paulo, Institute of Physics of São Carlos, São Carlos, SP, Brazil

University of São Paulo, Institute of Chemistry of São Carlos, São Carlos, SP, Brazil

Key-words: transition metal clusters, fullerenes, encapsulation properties

$Fe_6@C_{80}$



Transition-metal (TM) clusters inserted into fullerenes (C_m) have been considered as potential candidates for a wide range of applications, e.g., nanoelectronics, magnetic resonance imaging, due to their unique magnetic properties. Several experimental and theoretical studies have been performed, however, our current understanding of the interaction mechanisms of the TM with the inside fullerene surfaces that lead to the stabilization of those multicompounds is not satisfactory. In this work, we have employed DFT-PBE calculations to investigate the encapsulation of the small Fe_n, Co_n, and Ni_n (n = 4, 5, 6) clusters into spherical and oblate fullerenes C_m (m = 60, 70, 80, 90). We identified three key parameters that play an important role in the sign and magnitude of the encapsulation energy ($E_{enc} = E_{tot}^{TMn@Cm} - (E_{tot}^{TMn} + E_{tot}^{Cm})$): (i) The TM_n size and volume of the C_m cage. For example, the largest binding energy is found for the TM clusters inserted into C_{80} fullerene, while some of the $TM_6@C_{60}$ are unstable. (ii) The curvature of the inside C_n surfaces. (iii) The number of TM atoms that binds directly to the inside C_n surface. We found that due to the hybridization of the d-p states, that lead to the strong binding of TM clusters with the internal fullerenes surface, the total magnetic moments of many systems decrease compared with the respective bare clusters, e.g., changes from 6 μ_B for $Co_4@C_{70}$ to 10 μ_B for Co_4. Thus, we believe that our conclusions can help to improve the understanding of encapsulation of TM clusters inside fullerenes.

This work was supported by FAPESP

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

Hydrolysis of a VX-like Compound Catalyzed by the MgO(001) Surface

Raphael S. Alvim(PG)[1]*, Itamar Borges, Jr.(PQ)[2], Alexandre A. Leitão(PQ)[1]

[1] *Departamento de Química, Universidade Federal de Juiz de Fora Juiz de Fora, MG, 36036-330, Brazil.*

[2] *Departamento de Química, Instituto Militar de Engenharia, Rio de Janeiro, RJ, 22290-270, Brazil.*

Key-words: VX agent, adsorption, MgO(001), hydrolysis.

The VX agent, O-ethyl S-(2-diisopropylethylamino)ethyl methylphosphonothioate, is one of the main nerve agents, thus search for ways to deactivate it is considerably important. In this work, the hydrolysis and the adsorption reactions of a VX-like compound (O,S-dimethyl methylphosphonothioate, DMPT) on the MgO(001) surface were studied by density-functional theory (DFT) using periodic boundary conditions. A degradation mechanism involving six reactions was proposed and theoretically investigated. Conformations, free energy differences, transition state, reaction barriers and minimum energy paths were computed. We verified that the P-S bond, related to the agent toxicity, breaks through hydrolysis which can occur spontaneously throughout the analyzed temperature range (100-600 K). In the dissociative chemisorption of the DMPT molecule, the formation of intermediate MgO(001):$[SCH_3]^-$ $[PO(CH_3)(OCH_3)]^+$(s) is, from a temperature of about 495 K, thermodynamically less stable than the hydrolysis products. The possible reconstitution of the P-S bond does not occur according to a kinetic analysis - the electronic energy barrier for the direct formation reaction was 140.9 kJ/mol. After the recombination with the HO^- and H^+ ions, the $HOPO(CH_3)(OCH_3)$ and $HSCH_3$ products did not accumulate on the surface because these molecules desorb respectively above the 442.3 and 314.2 K temperatures. Therefore, 495 K is the necessary minimum temperature for not occurring the accumulation of the products on the surface, with the MgO reconstitution being the last step of the catalytic process.

Support: CAPES-Brazilian Ministry of Defense grant.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

Specific rotation to validate monosaccharide conformations

Renato R. de Andrade (PG), Clarissa O. da Silva (PQ)

Dequim, UFRuralRJ, Br 465, km 47 – Seropédica, Rio de Janeiro, CEP 23890-000.
Email: clarissa-dq@ufrrj.br, randrade@ufrrj.br

Key-words: Conformation of monosaccharides, optical rotation.

To study monosaccharide absolute conformations, it means, the information on conformation comprising the orientation of the hydroxyl groups[1], it was missing an experimental property able to distinguish among all possible hydroxyl group orientations. Using $[\alpha]_D$ calculations and a B3LYP/6-311++G(2d,2p) description[2], we can show in Figure 1 that the individual $[\alpha]_D$ values found for each representative conformation of xylose changes much less with the medium (gas-phase or solution) or basis sets, than for two different conformations, even when the difference between these two conformations is the orientation of only one hydroxyl group.

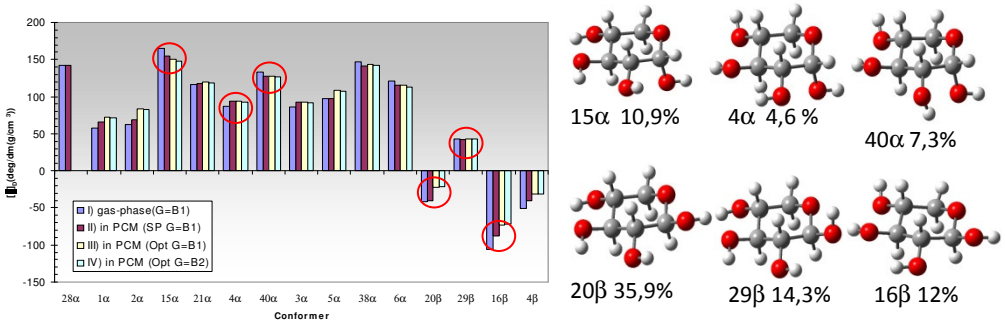


Figura 1: $[\alpha]_D$ values for the most stable stable conformers of D-xylose in different media and basis sets (B1=6-31+G(d,p) and B2=6-311+G(d)).

Additionally, the conformational sampling may be considered successful if the experimental optical rotation value of an aqueous solution of the respective monosaccharide is reproduced. This procedure was proven to work out for xylose[3], glucose[4] and levoglucosan monossacharides.

Support: FAPERJ e CAPES.

1- Andrade, R. R.; Silva, C. O. *Mini-Rev. Org. Chem.* **2011**, *8*, 239-248.
2- Stephens, P. J.; Devlin, F. J.; Cheeseman, J. R.; Frisch, M. J. *J. Phys. Chem. A.* **2001**, *105*, 5356-5371.
3- Andrade, R. R.; Silva, C. O. *Carbohydrate Research* **2012**, *350*, 62-67.
4- Silva, C. O.; Mennucci, B.; Vreven, T. *J Org. Chem.* **2004**, *69*, 8161-8164.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

Determination of Kinetics and Thermodynamic Parameters for the Ozonolysis of Isoprene in Multiconfiguracional Level

Rene Pfeifer(PG), Leonardo Baptista(PQ), Alexandre da Braga Rocha(PG), Graciela Klachquin (PG)
Federal University of Rio de Janeiro

Key-words: isoprene, Ozonolysis, MCSCF, TST

Biogenic Volatile Organic Compounds play an important role in tropospheric chemistry, mainly in the oxidative processes which lead to the formation and consumption of ozone an also to the production of Secondary Organic Aerosol (SOA). An important class of these compounds is the terpenes. Recent works[(1)] show great interest in how terpenes oxidations leads to the formation of SOA. Since isoprene is the most emitted biogenic organic compound, the study of the reactions of its ozonolysis has great value and represents a significant gain on the understanding of this system, since there some doubts about the structure of Criegge Intermediates form (birradical or zwiterrion). Isoprene has two different double bounds conjugated leading two different paths according to Criegge Mechanism [(2)].

In this work, the goal concern in estimate trust thermodynamics and kinetic parameters, using quantum mechanics methods to model the first step of isoprene oxidative reactions with ozone in gas phases, which are the rate determinant step.

Each geometry were optimized without geometry restriction and characterized as a minimum with all real frequencies or a transition state with only one imaginary vibrational frequency which confirms the first-order saddle point configuration. All calculations were performed using Multiconfiguracional Consistent Field (MCSCF) and Multireference Pertubation Theory (MRPT) and a double-zeta Dunning basis in GAMESS 2008 program [(3)].

A total rate coefficient is 1,9 x 10^{-16} cm^3 $molecule^{-1}$ s^{-1} was calculated for ozonolysis addition to isoprene. This value is ten times higher than the experimental rate coefficient (1,3 x 10^{-17} cm^3 $molecule^{-1}$ s^{-1}) [(4)] , indicating that a further refinement of the calculations is needed.

References:

1) Y. Shu, R. Atkinson, *International Journal of Chemical Kinetics*, 1994, 26, 1193.
2) Criegge, R.; Werner, G. *Liebigs. Ann. Chem, Karlsruhe,* 1949, 564, 9.
3) GAMESS 08 - M.W.Schmidt, K.K.Baldridge, J.A.Boatz, S.T.Elbert, M.S.Gordon, at el all ; *J.Comput.Chem.* **1993**, 14, 1347.
4) Neeb, P.; Moortgat, G.K, J. Phys. Chem. A, **1999,** 103, *9003*.

Support: FAPERJ, CNPq, CAPES, PGQu

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

"New crystal structures identified for platinum oxides using Density Functional Theory calculations[1]"

Ricardo K. Nomiyama(1), Maurício J. Piotrowski(2), Juarez L. F. Da Silva(3, 1)

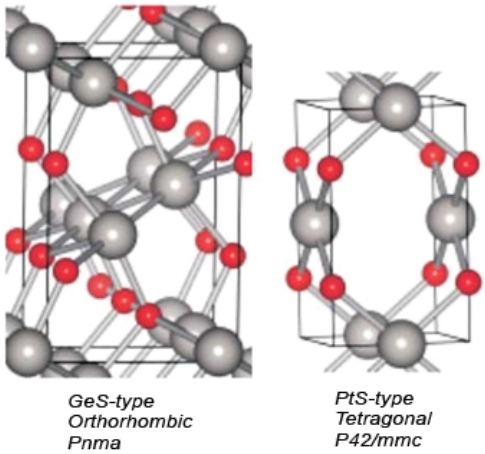
[1]*Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, SP.*

[2]*Departamento de Física, Universidade Federal de Santa Maria.*

[3]*Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, SP.*

Key-words: platinum oxide, crystal structure, density functional theory.

Platinum is an expensive material and it has an important role in catalysis and electrochemistry. The direct interaction of oxygen species with Pt surfaces of films and nanoparticles can lead to the formation of thin layers of platinum oxides (PtO_x) on the Pt surfaces, which can affect the reactivity for several chemical reactions. Thus there is a great interest to understand the atomic structure of thin PtO_x layers on Pt surfaces. To contribute to the understanding of thin PtO_x layers, we propose to use ab-initio calculations to study the atomic structure of bulk PtO_x oxides and its dependence with the local environment employing different crystal structures, which can be considered as model systems to understand the interaction of Pt-O. Therefore, in this work, we report a density functional theory study of the atomic structure of bulk PtO_x ($1 \leq x \leq 2$) employing the projected augmented wave method as implemented in the VASP code. To obtain the equilibrium volumes of platinum oxides, we optimized the stress tensor and the atomic forces on every atom. From our calculations, we identified a lowest energy structure (GeS-type, orthorhombic, Pnma space group) for PtO, which is 0.18 eV lower in energy than the structure suggested by Moore and Pauling (PtS-type, tetragonal, P42/mmc), see Figure. Furthermore, two crystal structures were identified for PtO_2, which are almost degenerate in energy with the lowest energy structure reported so far for PtO_2 ($CaCl_2$-type). Based on our results and analysis, we suggest that Pt and O atoms tends to form octahedron motifs in PtO_x even at lower O composition by the formation of Pt-Pt bonds. Therefore, we strongly believe that our approach helps to improve our understanding of PtO_x oxides.



GeS-type Orthorhombic Pnma *PtS-type Tetragonal P42/mmc*

[1] R. K. Nomiyama, M. J. Piotrowski, and J. L. F. Da Silva. Phys. Review B **84**, 100101(R) (2011).

Support: FAPESP.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

"Incorporation of Hydrogen in Molybdenum Carbide, a Theoretical Study"

Ricardo R. Oliveira (PG), Alexandre B. Rocha (PQ)

Departamento de Fisico-Química, Instituto de Química, UFRJ, Rio de Janeiro, RJ

Key-words: Molybdenum, Carbide, Incorporation of Hydrogen

Molybdenum carbide has presented a performance in hydrogenation of benzene comparable to noble metals [1,2]. The catalyst is deactivated after several hours of reaction. It was recently shown [2] that this deactivation is promoted by strong adsorption of benzene on catalyst surface, which is avoided as long as the hydrogen is available on surface. The goal of this work is to understand the ways by which hydrogen is incorporated to the carbide structure. We are performing DFT calculation with PBE exchange-correlation functional, combined with periodic boundary condition, plane waves basis set and pseudo-potentials on the orthorhombic Mo_2C. Energies for incorporation of hydrogen on the bulk and surface of molybdenum carbide are reported. Thermodynamics analysis for bulk is based on this formula:

$$\Delta E = E_{bulk+H} - (E_{bulk} + NE_H)$$

and for surface:

$$\Delta E = E_{Mo_2C+H} - (E_{Mo_2C} + NE_H)$$

Results show that the adsorption of hydrogen on the surface is favorable while its incorporation in the bulk is not. This indicates that the incorporation of hydrogen is consequence of carburization process, which is in agreement with some experimental findings.

[1] A.S. Rocha, V. Teixeira da Silva, A.C. Faro Jr., Appl. Catal. A 314 (2006) 137.
[2] A.S. Rocha, A.B. Rocha, V. Teixeira da Silva, Appl. Catal. A 379 (2010) 54.

Support: CNPq, PGQu

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

"Formation reaction mechanism of free hydroxyls on brucite - $Mg(OH)_2$ - layers"

Viviane S. Vaiss[1] (PQ), Itamar Borges Jr.[2] (PQ), Alexandre A. Leitão[1] (PQ)

[1]*Departamento de Química*

Universidade Federal de Juiz de Fora

Juiz de Fora, MG, 36036-330, Brazil

[2]*Departamento de Química*

Instituto Militar de Engenharia

Praça General Tibúrcio, 80, Rio de Janeiro, RJ, 22290-270, Brazil

Key-words: layered hydroxides, hydroxyls, DFT, reaction mechanism

Has been recently reported that surface and interlayer hydroxyl anions of reconstructed layered double hydroxides exhibit a strong basic character, therefore, it could act active sites in several base-catalyzed reactions. In this work, we used DFT calculations with periodic boundary conditions to investigate formation reaction mechanisms of free hydroxyls on $Mg(OH)_2$ layers. Two hypotheses for the hydroxyl formation were proposed and tested. In the firrst, a Mg(OH)2 layer hydroxyl migrates to the surface and in the second, a water molecule reacts with the Mg(OH)2 layer. The result in both cases is the formation of hydroxyl anions and a hydroxyl vacancy in the positively charged brucite layer. The global reaction is the same in both cases and the corresponding computed Gibbs free energy variation (ΔG) equaled 37.5 kcal/mol. The reaction barrier for the formation of hydroxyl anions on the $Mg(OH)_2$ surface, originating from the H_2O molecule dissociation, is lower than the reaction barrier for the direct formation of hydroxyl anions resulting from the $Mg(OH)_2$ dissociation. Therefore, it is expected that the formation of the hydroxyl anions on layered hydroxide involves the reaction of water molecules with the hydroxyl layers. These water molecules act as catalysts of the reaction.

Support: CAPES-Brazilian Ministry of Defense and a Vale S.A. (CEX-RDP-00138-10) FAPEMIG.

Theoretical Chemistry in Rio
Meeting to honor the 65th birthday of Prof. Marco A. Chaer Nascimento
Rio de Janeiro, June 11th and 12th 2012

Theoretical and experimental investigation of the disordered quaternary oxide $CoMo_{0.5}W_{0.5}O_4$

Author

Y. E. Licea[1], L. A. Palacios[2], J. G. Eon[1], A. Faro Jr.[1], R. Grau-Crespo[3]

[1]*UFRJ, Rio de Janeiro, Brasil*

[2]*UERJ, Rio de Janeiro, Brasil*

[3]*UCL, 20 Gordon Street, London, UK*

Key-words: Ab initio thermodynamics, Oxidative dehydrogenation, Oxygen vacancies, DFT, EXAFS, Rietveld refinement, Cation disorder

DFT calculations, EXAFS and synchrotron-light XRD techniques have been used to determine the solid structure and thermodynamic of mixing of a trimetallic wolframite oxide. The chemical formulae $CoMo_{0.51}W_{0.49}O_4$ has been determined from Rietveld refinement of synchrotron-light XRD data. From EXAFS simulation it could be conclude that oxygen in the first W(Mo) coordination shell are distributed as in the wolframite pure phase lattice. The theoretical calculation of Gibbs free energy of mixing, using the SOD [1] and VASP [2] codes, predicts a thermodynamically favorable wolframite-like structure solid solution which is disordered at all temperatures of interest, with a slightly negative enthalpy of mixing (Figure1). Calculation of vacancies formation energies in all oxygen different asymmetric position of a 2x2x2 super cell have shown that electrons are dislocated toward Mo atom after oxygen vacancies formation and also that these vacancies are energetically favored by Mo incorporation from x=1 to x=0 in the $CoMo_xW_{(1-x)}O_4$ wolframite phase system (Figure2), concluding that no synergetic between Mo and W but a linear effect would explain its catalytic behavior on propane ODH reaction.

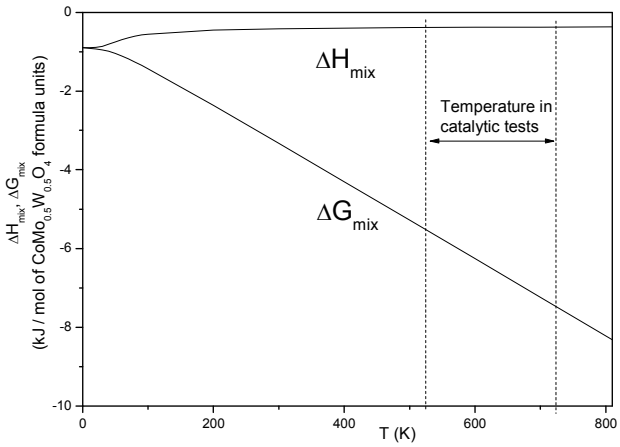


Figure1. Enthalpy and free energy of mixing for $CoMo_{0.5}W_{0.5}O_4$ solid solution

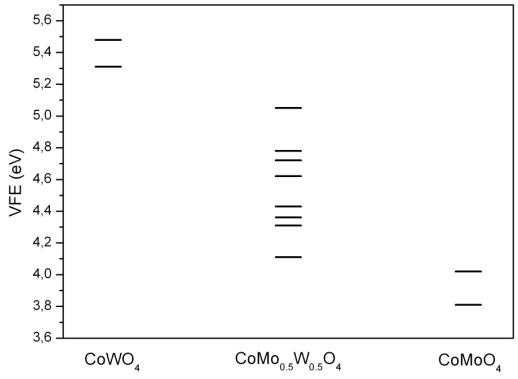


Figure2. Vacancy formation energies for three wolframite phases.

References:

[1] R. Grau-Crespo, S. Hamad, C.R.A. Catlow and N. H. de Leeuw. *J. Phys. Cond. Mat.* , **19,** 256201 **(2007)**

[2] Kresse G and Joubert D **59** *Phys. Rev. B* 1758 (**1999**)

Support: LNLS, PETROBRAS, UCL