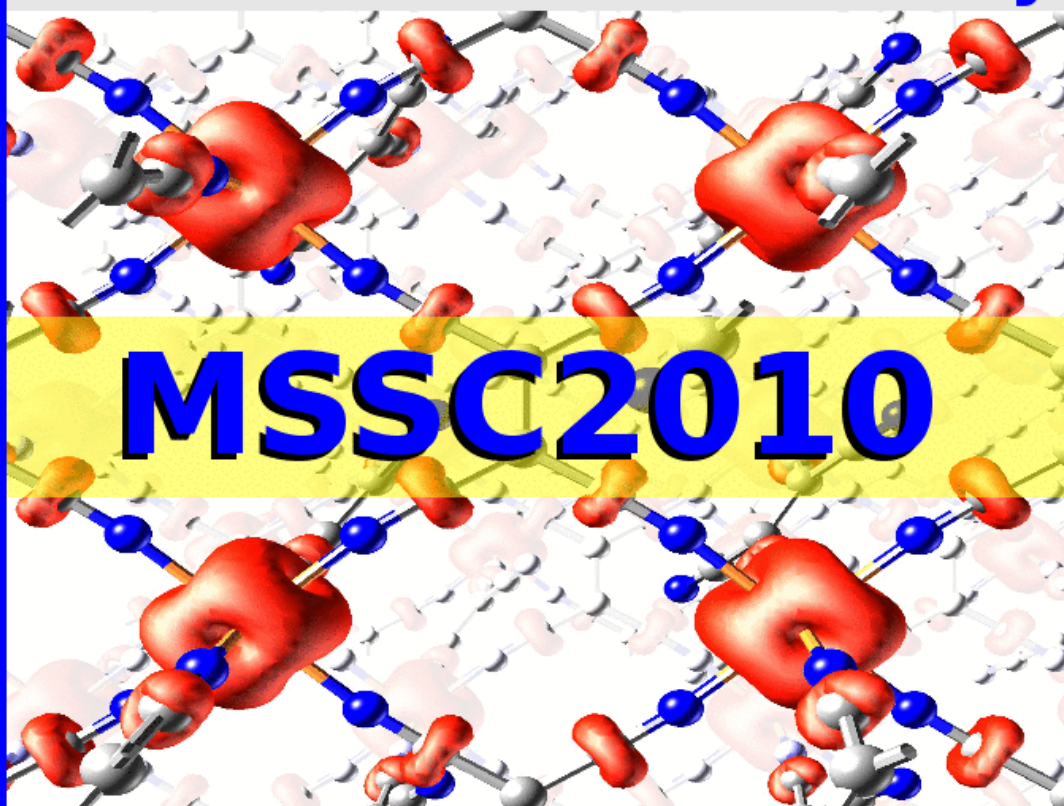


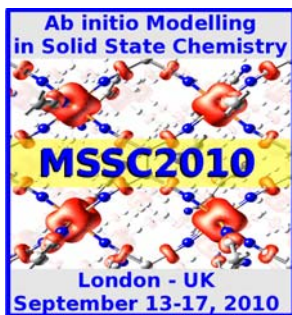
**Ab initio Modelling
in Solid State Chemistry**



MSSC2010

**London - UK
September 13-17, 2010**

**POSTER
ABSTRACTS**



Ehsan Ahmad

Imperial College London

**Quantum Mechanical Simulations of the
Electronic Structure and Thermodynamics
of the Manganese Oxides**

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Anthony Kucernak, Nicholas M Harrison.

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In recent years there has been a growing interest in the use of perovskites for application in fuel cells, particularly in solid oxide fuel cells [1] where they have been implemented as anode, cathode [2] and electrolyte [3] materials due to their catalytic and ion conducting properties. Some of the latest work has involved exploring their use as cathode catalysts in alkaline fuel cells [4] where high activity has been shown for the oxygen reduction reaction one of the biggest obstacles to improving performance. In this respect an interesting ability of perovskites is that any modification of the compositional atoms and their stoichiometric ratios will lead to differing degrees of catalytic activity, the understanding of which is one of main factors motivating the proposed study.

The crystal structures of the LaMnO₃ and its competing Mn Oxides (MnO, MnO₂, Mn₂O₃ and Mn₃O₄) have been calculated using hybrid exchange density functional theory, as implemented in the CRYSTAL09 package [1,2]. We present the calculated electronic properties of the bulk structures as well as the calculated phase diagram and Gibbs free energies of formation which are compared to those obtained experimentally.

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Luigi Bagolini

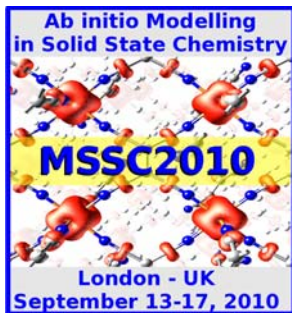
"La Sapienza" University of Rome

Quantum Confinement Phenomena
in Nanocrystalline Silicon

We predict theoretically and prove experimentally the occurrence of quantum confinement in hydrogenated nanocrystalline silicon. We prove that only valence states (positively charged carriers) are confined effectively within the nanograins.

The emission associated to confined states is verified by photoluminescence experiments on nanocrystalline samples with controlled grain size.

According to present study we propose nanocrystalline silicon as a promising material for oxygen free optoelectronics, silicon based memories and photovoltaics.

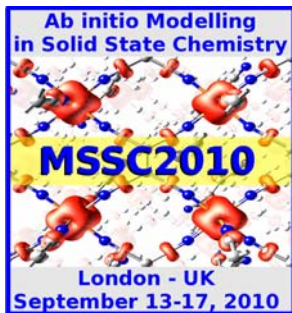


Robert Brown

Georgia Institute of Technology

**Electron-vibration Coupling in
Organic Semiconductor Crystals**

We discuss the basic processes by which the charge-carrier mobilities in organic semiconductor crystals are impacted by intra- and inter-molecular vibrations.



Su Chew

Imperial College London

An Ab Initio Study of CuGaSe₂ (001) Surface

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The chalcopyrite material makes one of the best performing devices for heterogeneous polycrystalline thin film solar cells. Specifically, the In-rich Cu(In,Ga)Se₂ solar cell has reached efficiencies of approximately 19% ^[1]. Despite this, many of the fundamental properties of this material remain unexplained. In principle, theoretical efficiencies of CuGaSe₂ solar cells should be close to those of Cu(In,Ga)Se₂. However, current efficiencies in CuGaSe₂ solar cells are of the order of 9.5% ^[2]. More research is needed to employ this material in photovoltaic applications.

Density Functional Theory (DFT) calculations using B3LYP hybrid exchange functional ^[3] were performed in the CRYSTAL code ^[4] to investigate the atomic and electronic structure of the CuGaSe₂ (001) surface. Experiments such as low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) have shown that the (001) surface of CuGaSe₂ has a (4x1) reconstruction, and that it has Cu-poor and Se-rich surface stoichiometry ^[5], ^[6]. The structural richness of the chalcopyrite increases the possibility for engineering the CuGaSe₂/CdS heterogeneous interface by surface control during growth.

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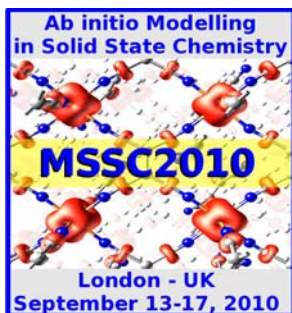


Damilola Daramola

Ohio University

Computational Analysis of Solid Oxide Fuel Cell Components

SOFCs operate at high temperatures with recent research focused on increasing efficiency in the presence of H₂S. Computational modeling was performed on crystal structures that make up a typical SOFC as a preliminary condition to modeling gas component interactions with the cell.



Pamela Finke

Universitaet Bremen

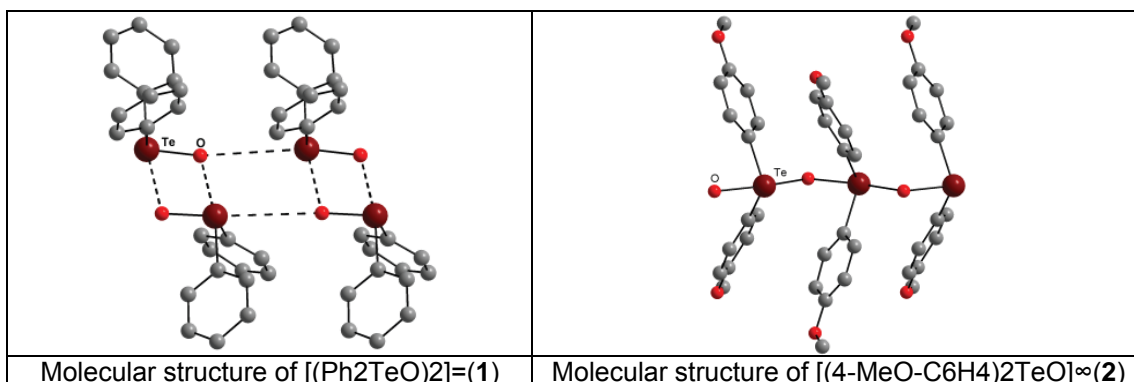
Heavy p-block Organo Element Oxides

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Secondary interactions are a widespread phenomenon in the chemistry of heavy main group elements and are often essential for the supramolecular alignment of individual molecules in the crystal lattice. In this case study we focus on secondary interactions of molecular tellurium oxides. The crystal structures of these compounds are well known and the number of secondary interactions within them is limited.

The diaryltelluriumoxide $[(\text{Ph}_2\text{Te}=\text{O})_2]_\infty$ (1) consists of individual Ph_2TeO molecules (av. Te-O bond length 1.89 Å), which are linked by secondary interactions to give rise to a four-membered Te_2O_2 ring structure (av. $\text{Te}\cdots\text{O}$ distance 2.55 Å). A second set of secondary interactions builds up a polymeric structure (av. $\text{Te}\cdots\text{O}$ distance 3.77 Å).¹ In contrast, the crystal structure of the diaryltelluriumoxide $[(4\text{-MeO-C}_6\text{H}_4)_2\text{TeO}]_\infty$ (2) contains no ring structure, but a one-dimensional polymer with alternating Te-O single bonds (2.02 and 2.10 Å)²

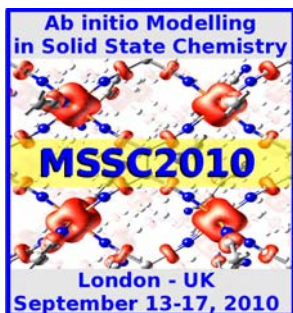


In a combined gas-phase and solid-state DFT study we are investigating the stepwise formation from the molecules, via dimers and tetramers, to polymers of the two different diaryltelluriumoxides. Elongations of selected crystallographic axis in the crystal lattice are undertaken to establish the scope of the secondary interaction. In preliminary gasphase calculations we found, that the scope in the $(\text{Me}_2\text{Te}=\text{O})_2$ dimer is greater than the sum of the van der Waals radii ($\text{rvdW}(\text{Te}) + \text{rvdW}(\text{O}) \approx 3.6 \text{ \AA}$). In comparison we also

calculated the PES of the dimerisation of $(\text{Me}_2\text{Te}=\text{O})_2$ by wavefunction-based methods like MP2 and coupled-cluster.

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Simon Grabowsky

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The Electronic Nature of the Epoxide Ring Revealed by Topological Analyses of Electron Density and Electron-Pair Localisability

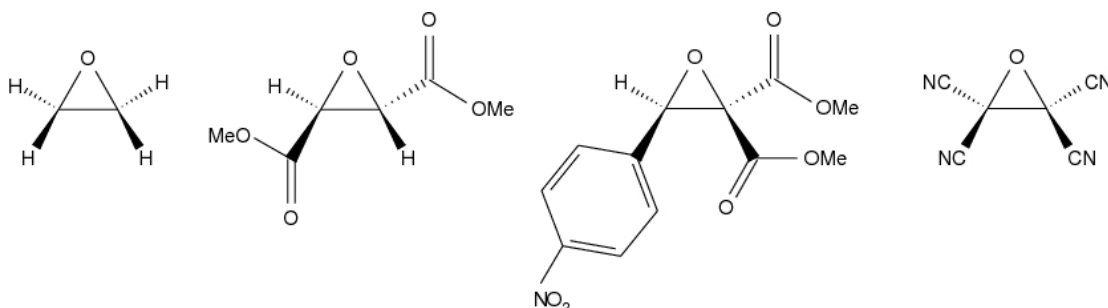
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The electronic situation in ethylene oxide (oxirane, epoxide) is special in chemistry due to the high ring strain. From geometrical considerations and MO theory, the bonds in the three-membered ring have been described as outwardly bent, but there is no experimental verification yet.

We synthesised and crystallised a row of epoxide derivatives with electron-withdrawing substituents (compounds 1-4, see Figure). High-resolution single-crystal X-ray diffraction experiments at low temperatures (25K-100K) were carried out at the synchrotron beamline F1 of HASYLAB/ DESY and at a conventional Mo source.



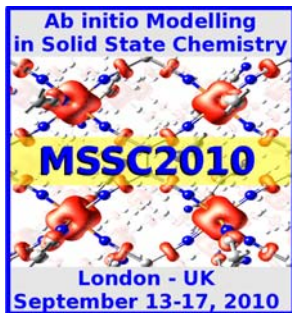
From the experiment, we determined the electron-density (ED) distribution (multipolar modelling¹) and the electron localizability indicator (ELI) (constrained wavefunction fitting²) and analysed them with respect to the bonding situation in the three-membered ring³. In addition, quantum chemical ab-initio calculations were carried out in the gas phase and within periodical boundaries (programmes GAUSSIAN 03 and CRYSTAL 06) to obtain ED and ELI from theory, too.

In recent pharmaceutical research, oxirane derivatives have been found to be of potential anticancer activity⁴. Cpds. 2 and 4 serve as model compounds for protease inhibitors⁵, which makes it important to investigate substituent effects on the electronic situation in the epoxide ring.

Results show that the outwardly bent bond character can only be confirmed unambiguously in the ELI (localisation of electron pairs), but not in the ED (concentration of electrons). In the geometries, the ELI, and the ED, substituent effects can be quantified with increasing strength from cpd. 1 to 4.

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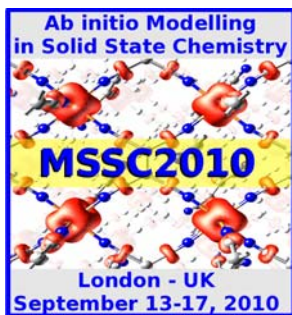


Denis Gryaznov

University of Latvia

**Density Functional Theory Calculations
on Phonon Properties in SrTiO₃ and LaCoO₃**

Density functional theory (DFT) calculations on phonon properties in two perovskite-like materials are presented. Namely, SrTiO₃ and LaCoO₃ are considered due to important practical applications like oxygen sensors and solid oxide fuel cells. The calculations on both materials were performed using Crystal code. The materials distort to tetragonal and rhombohedral lattice structures as the temperature goes down for SrTiO₃ and LaCoO₃, respectively. However, the rhombohedral phase of LaCoO₃ was only considered in the present study as being stable in a wide temperature range. It also requires a comparison of different magnetic states in LaCoO₃. In contrast, SrTiO₃ has an anti-ferro distortive transition to tetragonal phase at ~100 K. Thus, the phonon frequencies were determined in cubic and tetragonal SrTiO₃. The calculations included a comparison of standard and hybrid DFT functionals for a number of properties like lattice parameters, band gaps, atomic charges, and phonon frequencies. The results were also compared to experiments and other theoretical literature data.

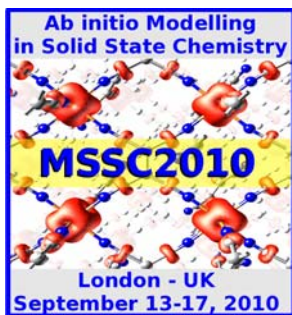


Davood Habibi

The Bu Ali Sina University

**An Efficient Method for the Synthesis of
Phthalhydrazide Derivatives in Solvent and
Solventless Microwave-mediated Conditions,
Investigation of their Diels-Alder Reactions
as well as the Ab Initio Calculations of the
Products Stabilities**

Different phthalhydrazide derivatives were synthesized from the reaction of phthalic anhydrides with hydrazine dihydrochloride in acetic acid or solventless microwave-mediated conditions. Tendency of the products with thiophene in Diels-Alder reactions was investigated as well. The Ab initio calculations showed that the stability energy of the cis products is roughly as same as the trans.



Venkatesha Rama Hathwar

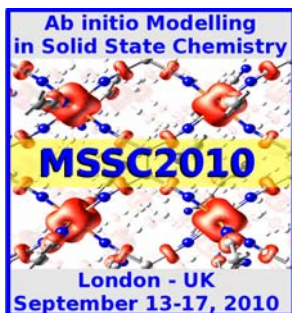
Indian Institute of Science

Topological Features of Short Halogen... Halogen Contacts via Experimental and Theoretical Charge Density Analysis

Studies on halogen...halogen contacts in organic compounds using ab initio calculations¹ and crystallographic studies² show that these interactions are controlled by electrostatics. Indeed, these are represented as C-X1...X2-C moieties (where $\#1=C-X1...X2$ and $\#2=X1...X2-C$; $R_{ij}=X1...X2$ distance). Cl...Cl contacts are directive and are either attractive or repulsive based on the geometry of contact.² In order to decipher the specific interaction profiles of Cl...Cl, Cl...F and F...F contacts in the presence of other weak hydrogen bonds, charge density analysis of 2-chloro-3-quinolinyl methanol, 2-chloro-3-hydroxypyridine, 2-chloro-3-chloromethyl-8-methylquinoline, 2-chloro, 4-fluoro benzoic acid, 4-fluoro benzamide have been carried out using high resolution X-ray diffraction data (resolution, $\sin\theta/\lambda = 1.08 \text{ \AA}^{-1}$) collected on good quality crystals at 100 K. The intermolecular interactions were analyzed based on Bader's QTAIM theory³ incorporated in XD2006 package.⁴ Theoretical calculations of charge density analysis were carried out using CRYSTAL06⁵ for the comparison of observed results. The halogen...halogen short contacts are observed as a 'closed shell' van der Waals interaction with the (3, -1) bond critical point. Topological features of Type II contacts suggest a nucleophile-electrophile interaction as observed earlier.⁶ Type I contacts are found to be more repulsive in their electronic distribution when compared to Type II contacts. Further, the nature of contacts in the case of Cl...F and F...F interactions are discussed in the context of Cl...Cl interactions.

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Guillermo Hernandez

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**Theoretical Study of the Crystalline Structure
for the CaV₂O₄, and their Electronic,
Magnetic and Vibrational Properties**

CaV₂O₄ is a crystalline material with interesting magnetic properties due to the arrangement of its magnetic V³⁺ ions. Recent investigations on CaV₂O₄ have been conducted by employing one-dimensional models to describe the electronic interactions within the V³⁺ zig-zag chains. In contrast, a theoretical study on the structural, electronic, magnetic, and vibrational properties of CaV₂O₄ by means of quantum-mechanical calculations on 3D periodic models is presented in this work. All the calculations were carried out with the program CRYSTAL06 using the B3LYP functional and all-electron split valence Gaussian-type basis sets as the level of theory. Two magnetic phases of the CaV₂O₄ system were considered for the study, namely: the ferromagnetic (FM) and the antiferromagnetic (AFM). The computed structural parameters are in good agreement with experimental x-ray data. Regarding the electronic properties, the Mulliken population analysis as well as total electronic density and spin density maps showed that the magnetic ions are in a covalent environment and share electrons with their neighboring oxygen atoms. Moreover, differences between the band structure of the FM and AFM phases of the material suggested that significant interactions between the material chains could exist. Finally, the computed vibrational properties allowed us to classify the 32 IR-active normal modes of the crystal in four types.



Romi Kaur

Imperial College London

**A Hybrid Exchange Density Functional Study
of CrO₂ as a Spin Polarised Material for Spintronics**

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2. *Computational Science and Engineering Department, STFC Daresbury Laboratory, Cheshire WA4 4AD, UK.*

Theoretically, Chromium Dioxide has been predicted to be 100% spin polarised. However, the development of devices exploiting its half metallicity has been problematic. Magnetic Tunnelling junctions based on epitaxial CrO₂ films exhibit a low magnetoresistance^[1-4]. Epitaxial films experience tensile stress due a mismatch of lattice parameters with the substrate or barrier layer. CrO₂ is generally deposited on a range of substrates such as TiO₂^[5] and Al₂O₃^[6]. The mismatch of lattice parameters affects the local strain at the interface and could potentially modify the structural, electrical and magnetic properties of the film. Therefore, it is vital to understand the effect of strain, σ on heteroepitaxial structures in order to provide an explanation for the poor performance of hybrid spin transport devices based on CrO₂. Here, we investigate the effects of strain due to a distortion of the lattice parameter(s) on the electronic properties of bulk CrO₂. Hybrid exchange Density Functional Theory calculations have been performed using CRYSTAL, a periodic quantum mechanical code based on the use of Gaussian functions.

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Leandro Liborio

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**Defect Chemistry and Photoluminescence
in Chalcopyrites: the Case of CuAlS₂**

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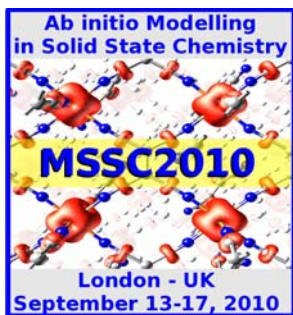
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In this work we have used hybrid density functional theory to study the wide band gap chalcopyrite copper aluminium di-sulfide: CuAlS₂. CuAlS₂ is a prospective material for the development of wide-band gap photovoltaics (WBGP). WBGP have reduced losses due to series resistances, are better suited for spatial applications and are more efficient at lower intensities ^[2]. Moreover, CuAlS₂ is a promising candidate for building light-emitting devices that operate in the visible and ultraviolet spectral range ^[3]. Following the methodology known as ab initio thermodynamics ^[1], we have calculated the formation energies of charged and neutral intrinsic defects at different environmental conditions. According to our results, CuAlS₂ is a p-type material that cannot be type inverted through the formation of intrinsic defects. Moreover, we have predicted the existence the CuAl₈S₅ ordered defect compound (ODC) that is originated by the complex defect (2V_{Cu}¹⁻+Al_{Cu}²⁺) formed by copper vacancies and aluminum substitutionals. Hybrid functionals allowed for an accurate calculation of the band gap states associated with the different intrinsic defects, and these states were used to study the origin of the CuAlS₂ photoluminescence emissions. Our results suggest that the (2V_{Cu}¹⁻+Al_{Cu}²⁺) defect is responsible for the orange photoluminescence emission, whereas the ultraviolet emissions are mostly due to the V_{Cu} defect.

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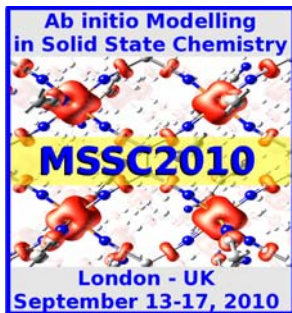


Madhubhashini Makehelwala

University of Peradeniya

Probing Reactivity Sites on Pyrite – Oxidative Interactions with 4-chlorophenol

In the present work we experimentally examined the oxidative interactions of 4-chlorophenol (4-CP) onto pyrite surface with the help of DR-FTIR spectroscopy. All experiments were carried out in gas phase under ambient atmospheric conditions to enhance adsorption of the 4-CP onto pyrite surface. The interactions of 4-CP with pyrite sites were examined using cluster modeling approach using several density functional methods. Surface complexes optimized using the Harris and Perdew-Wang local functionals were close to both experimental data and structures optimized using the nonlocal Becke-Lee-Yang-Parr (BLYP) functional. Binding energies calculated with the gradient corrected BLYP functional were only weakly dependent on the method used for geometry optimization.



Ruth Martinez-Casado

Imperial College London

Quantum-Mechanical Study of He-atom Diffraction from Metal-Oxide Surfaces

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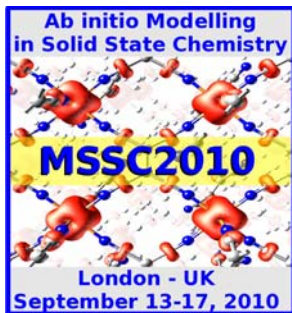
He-atom scattering from surfaces is a well established and valuable tool for characterizing the structure of periodic surfaces, determining gas-surface interaction potentials, and investigating the presence of defects and adsorbates. Unlike other techniques (e.g., LEED, STM or FIM), He-atom scattering causes no damage to the surface, is very surface sensitive, as it probes only the outermost layer, and does not suffer from the surface charging effects, which plague, for instance, photoelectron spectroscopy and electron diffraction. The correct interpretation of the experimental data requires a quantum treatment of the He-surface interaction potential.

Empirical models of the surface atom potential, which introduce an uncontrolled approximation to the interpretation of the data, have been used but are limited to few systems, where interactions are reasonably well understood^[1]. A quantum-mechanical description of the interactions has not previously been possible, because the dominant methodologies for dealing with extended systems are based on Hartree-Fock (HF), density functional theory (DFT) and/or hybrid exchange DFT approaches, which do not describe correctly dispersion forces, vital for the scattering process. In our most recent work^[2], we show that a qualitatively correct description of the He-surface interaction potential can be obtained by using and/or implementing novel, beyond HF-based *ab initio* techniques.

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Rationalisation of the Infra-Red Frequencies of Brønsted Acid Sites in the MIL-53 MOF Material: Role of the Pore Size and the Nature of the Metal Center

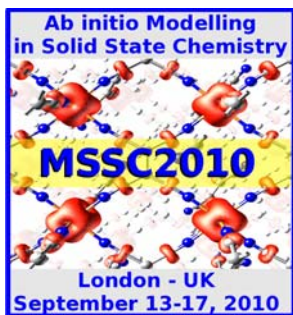
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F. Millange³ T. Devic³ G. Férey³ and C. Serre³

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Nanoporous Metal organic frameworks are constituted by inorganic subunits connected by organic linkers. The most interesting feature of these materials relies on the wide variety of metals, inorganic moieties and functionalized organic linkers that could be assembled to form different pore size and connectivity. That makes these compounds very promising for various applications including electrochemistry, CO₂ storage, drug encapsulation and controlled release. These structures represent a challenge for theoretical chemistry as they contain organic and inorganic parts, implying strong and weak interactions, which both require specific attention. Our aim was at probing the acidity of the μ -2-OH groups present at the surface of a series MIL-53 (M=Al, Fe, Cr, Al, Ga) solids and further exploring the MIL-53(Fe)/drug interaction. To properly describe these systems, DFT and DFT + U approach was employed depending on the metal correlations associated with the semi-local PBEsol functional. The results obtained using this novel functional is compared to those considering the PBE-D which includes Grimme correction for dispersion. Our first results show a good agreement between the experimental and simulated large pore forms for each investigated MIL-53(M) solid. The pore size of the narrow pore form seems to be governed by van der Waals weak interactions that affect the vibrational frequency of the μ -2-OH acid site.



Sahar Nazer

University of Tehran

Conformation Analysis of N–Acetyl Cysteine by ab initio Calculations

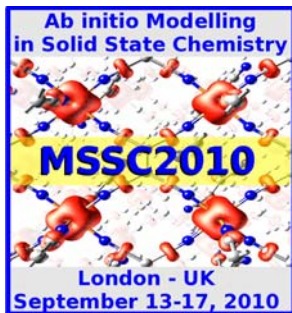
N - acetyl cysteine (NAC) is the acetylated form of L-cysteine. It is a metabolite of the Sulfur-Containing amino acids. NAC is an antioxidant that increases intracellular glutathione at the cellular level. NAC is an agent being investigated as a possible chemo preventative agent based on its antioxidative/detoxifying properties and laboratory studies have shown a decrease in induced lung tumours in mice using this agent.¹ It is interesting that NAC, a Food and Drug Administration-approved drug for treatment of acetaminophen toxicity, prevents toxic damage to the liver by a benzoquinone derivative of that drug.^{2, 4} In addition, NAC has also been used to reverse mutagenic^{3, 4} effects of particulate air pollutants in rat lungs

Since, the biological active molecules must have a specific stereochemistry so ab initio calculations at the HF/ 6-31 G* level of theory for geometry optimization and MP2/ 6-31 G*/HF/6-31 G* for a single point total energy calculation are reported for the important different conformations of N-acetyl cysteine. This study was undertaken in order to calculate geometry optimized structures and conformational isomer energy differences of N - acetyl cysteine.

According to these calculations, there are 10 conformations for NAC and four conformers of them are more stable than the others. The minimum energy conformation A is the most stable form. It is apparently, the shown hydrogen bonding in structure A is the most important factor for the stability of it.

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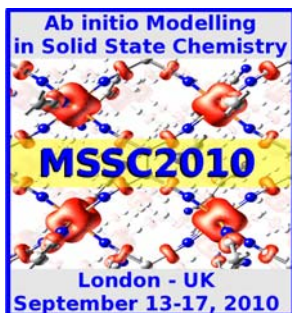
Protonic Defects and Water Incorporation in Si/Ge-based Apatites for Fuel Cell Applications

Mixed-metal oxides that show high ionic or mixed conductivity have attracted considerable attention owing to the potential applications such as solid oxide fuel cells (SOFCs). This includes the discovery of high oxide-ion conductivity in apatite-type materials based on $\text{La}_{10}(\text{MO}_4)_6\text{O}_{2-y}$ (where $\text{M}=\text{Si}$ or Ge)^[1]. Recently, water incorporation into apatite materials has been shown to enhance ionic conductivity at intermediate temperatures particularly in the germanate systems^[2]. However, there is still debate regarding the location of oxygen and OH defects, and the water incorporation reactions.

This presentation highlights recent work focusing on defect, transport and water incorporation mechanisms in $\text{La}_{10}(\text{SiO}_4 / \text{GeO}_4)_6\text{O}_{2-y}$ apatites, using computer simulation methods, which have been applied successfully to other complex ion-conducting oxides^[3, 4]

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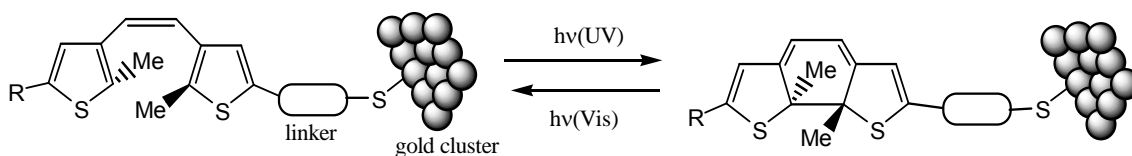
Optical Properties of Photochromic Molecules Functionalized by Gold Clusters: Towards Nano-Hybrid Switches

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There is a great interest in the development of electronic devices at the molecular level. In this context, organic photochromes are candidates of choice since specific changes in their electronic and structural properties occur under light irradiation. By carrying out information at the molecular level, these molecules can act as a memory or a switch. Among the various families of organic photochromes, diarylethene molecules are promising candidates for optical, electronic and plasmonic applications due to their interesting photochromic properties, i.e. good fatigue resistance and high thermal stability of closed and open forms.



*Scheme: photochromic equilibrium in diarylethene series
(R=SH, phenyl-SH, thiophene-SH, C=CSH...; linker= phenyl, thiophene...)*

However, in order to use these photochromic compounds within an active electronic device, it is necessary to make sure that their commutation properties are preserved when they are in contact with metallic electrodes. Recent studies have shown that the molecular structure of the diarylethene has a great impact on the reversibility mechanism. Thus, Dulic et al.^[2] studied the optical properties of photochromic molecules assemblies on a gold surface. UV-vis spectroscopic measurements show that in the case of photochroms with thiophene linkers functionalized by gold, the reaction of ring-opening was always possible whereas the cyclization reaction was inhibited.

Within the framework of the Density Functional Theory (DFT) and Time-Dependent DFT, we determined the spectroscopic properties of diarylethenes grafted on small gold clusters. The molecular orbital interactions between the

photochromic molecule and the gold cluster made it possible to rationalize some experimental findings.

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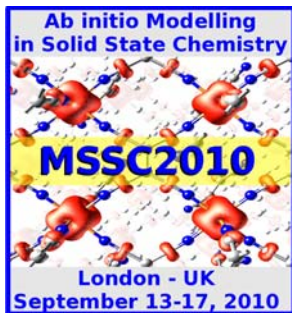


Victor Posligua

Universidad San Francisco de Quito

**Quantum-Mechanical Study of Crystal
Composed of Boron Nitride Nanoclusters [BiNi, i = 12]**

In this work, a quantum mechanical study of the B₁₂N₁₂ system using periodic models is presented to theoretically characterize this material and determine its potential applications.

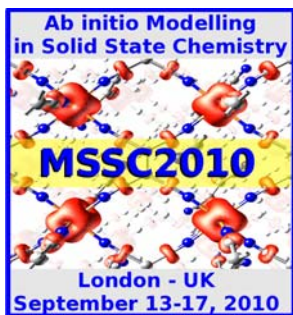


Claudia Quarti

Politecnico di Milano

Excitons in Organic Crystals
from First Principle Calculations

We use molecular exciton theory for the description of exciton formation and for the calculation of the excitonic band structure of p-NitroAniline, anthracene and 9,10-bis(phenylethynyl)anthracene crystals. The main features of the experimental UV-Vis absorption spectrum are predicted correctly.



Maria Carmen Ruiz Delgado

University of Malaga

Impact of Functionalization on the Charge-Transport Parameters of Organic Semiconductors

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Organics-based electronic devices share a common trait: their performance critically depends on the efficiency with which charge carriers (electrons and/or holes) move within the π -conjugated materials.¹ Thus, gaining a better understanding of the factors involved in the charge-transport mechanism is of great scientific and technological interest. Our theoretical work aims at providing strategies on how to optimize the key charge-transport parameters impacting charge mobility at the molecular level with the ultimate goal of improving the charge transport efficiency in (opto-) electronic devices. Here, the calculated electronic band structures and density of states of two of the most appealing families of n-channel semiconductors for organic field effect transistors-perfluoroacenes and perylene-tetracarboxylic-diimide (PTCDI) crystals, see Figure 1- are studied in detail using the CRYSTAL06 program. Our work suggests new design strategies and points to specific promising compounds for the development of high-performance electronic devices.^{2,3}

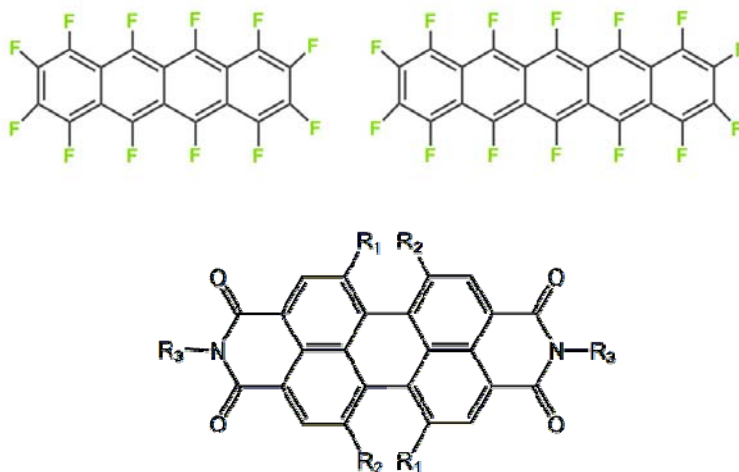
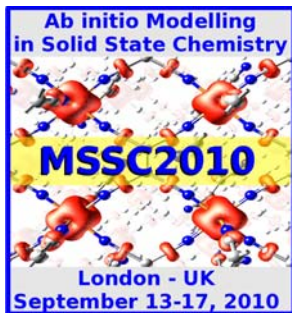


Figure 1. Chemical structures of perfluorotetracene and perfluoropentacene (top) and PTCDI systems (bottom) investigated in this study.

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Jessica Scaranto

University of Venice

**A Quantum-Mechanical Study of CHClF₂
Adsorbed on Anatase (101) Surface**

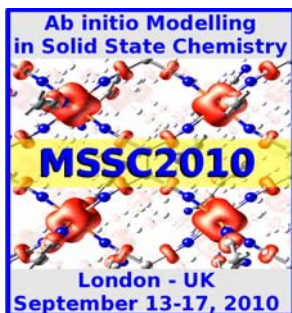
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Heterogeneous photocatalysis on TiO₂ represents a promising approach to solve the problems at the atmospheric level generated by the employment of HCFC. The study of the adsorbate-substrate interaction can be useful in order to develop successful applications. Here, we report the main results resulting from a quantum-mechanical simulation of chlorodifluoromethane (CHClF₂) adsorbed on the anatase (101) surface. The main aim is to obtain computed vibrational frequencies to compare with those observed at the experimental level. The calculations have been performed within the DFT level using the B3LYP exchange-correlation functional as implemented in the CRYSTAL program^[1]. The surface has been modeled using a relaxed 12-atomic layers slab; the molecule has been placed above it considering a (2 x 2) periodicity which corresponds to a surface coverage equal to 0.25 ML. The final adsorbate-substrate systems have been fully optimized by taking into account all the possible reasonable initial configurations. The obtained systems have been characterized from the energetic point of view computing not only the binding energy but also the interaction and distortion ones. The comparison between the calculated and observed frequencies suggests that the adsorption is possible through both the F and the Cl atom. Moreover, the molecule interacts also by an H-bond involving one surface Lewis basic site corresponding to the under-coordinated oxygen ion.

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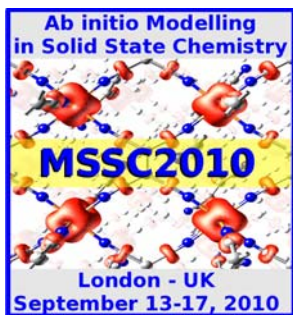


Christian Solis Calero

Universitat de les Illes Balears

DFT Studies on Phospholipids Mediated Decomposition of Hydrogen Peroxide

Hydrogen Peroxide molecules play a significant role in controlling certain cellular functions and its excess causes significant damage to biological systems. There is experimental evidence that its decomposition is accelerated above phospholipids membranes surface. We propose a mechanism for Decomposition of Hydrogen Peroxide on amine-phospholipid surface model based in Dmol3/DFT calculations. The model was built using periodic boundary conditions. Each unit cell contains two phospholipids molecules, two hydrogen peroxide and nine water molecules. The reaction proceeds by a polar heterolytic mechanism, amine –phospholipids lead to the polarization of the –O-O- bond in hydrogen peroxide, which allows the nucleophilic attack of an oxygen atom of a second hydrogen peroxide molecule. Overall, two hydrogen peroxide molecules react in a bimolecular reaction to yield an oxygen molecule and two water: $2 \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2 \text{H}_2\text{O}$. Our results show that can be hypothesized that cell membrane surface environment could enhance this reaction by a neighboring catalyst effect.



Messekine Souad

Chemin de Musée Perolle

**Adsorption of Water Molecule on Surfaces
of YVO₄: LCAO Calculations**

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² Department of Chemistry, University of Fribourg, Switzerland

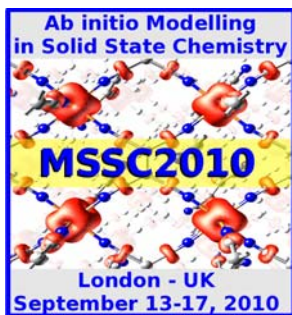
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LCAO simulations of surface properties and water adsorption on tetragonal zircon-type YVO₄ are performed using a slab model framework. Two slab models with the different surface termination were used for calculations. The optimized structures and water adsorption energies have been calculated for the various types of surface coverage.

It is shown that the formation of H-bonds between the water hydrogens and surface oxygens, as well as between the water molecules themselves, controls the structure of the water adsorption layers on YVO₄ surfaces.

Obtained results indicate that the water molecules were adsorbed dissociatively to the seven-fold oxygen coordinated 7c-Y site on the (010) surface of YVO₄

The adsorption energies of water molecule and geometries of the systems with adsorbed water molecules are reported in detail



Kouadri Moustefai Soumia

Hassiba Benbouali University of Chlef

Infrared Spectrum of Molecular Crystals Forming Inorganic Aerosols: Ab Initio Study of Ammonium Nitrate Phase IV

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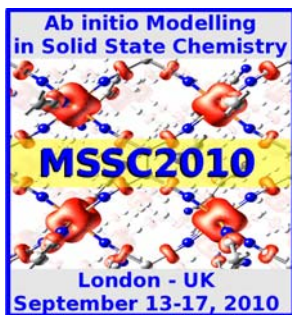
Atmospheric aerosols have an adversely effect on human health and significant consequences on regional and global climate changes. Ammonium nitrate (NH_4NO_3) is a common constituent of fine atmospheric aerosols, accounting for 10-30%^[1]. It is known that NH_4NO_3 solids can exist in five stable polymorphic forms under ambient pressure, depending on the temperature. Among these solid phases, phase IV is stable at the tropospheric temperature and is the only phase considered in current atmospheric chemical models^[2, 3].

In this work, the equilibrium structural parameters and vibrational frequencies of ammonium nitrate phase IV are calculated by using the periodic; ab initio program CRYSTAL06, which adopts an all-electron Gaussian-type basis set. Hartree-Fock (HF), local density (LDA), gradient-corrected (PW91), and hybrid (B3LYP) density functional have been used. All four functionals, B3LYP, LDA, PW91 and HF reproduce the equilibrium geometry of ammonium nitrate to a high level of accuracy compared to experiments^[4,5]; and show an overall similar results with previous plane wave, pseudo-potential calculations^[6]. The obtained structures of this system were used in the prediction of the vibrational frequencies. The maximum absolute deviation from the measured frequencies^[7,8] is about 5% for B3LYP indicating that this functional performs extremely well in this case compared to the deviation about 10% for both the LDA and PW91 functionals. The absolute deviation increases to 15% when the HF functional is used.

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Ab initio Investigation of the Electronic Structure and Magnetic Properties of a Hydrogenated Graphene Sheet

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First-principles calculations employing the hybrid exchange functional B3LYP are used to investigate the structural parameters, electronic structure and associated properties of a graphene, graphane and graphone sheet. The effect of different levels of hydrogenation, and thus the relative change in carbon hybridization, on the aforementioned properties is thus observed. Graphane is found to have a band gap corresponding to an electronic insulator at room temperature. Graphone is found to have a ferromagnetic magnetic ground state. The effect of strain on the graphone magnetic ground state was also investigated. Calculations show that the magnetic ground state can be tuned from ferromagnetic to antiferromagnetic by applying an appropriate degree of strain