

FA4-MS28-T01

Accurate ab initio calculation of the cohesive energies of molecular crystals. Lorenzo Maschio^a, Denis Usvyat^b. ^a*Università di Torino, Italy.* ^b*Universität Regensburg, Germany.*
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Molecular crystals certainly represent a tough challenge for the standard tools of modern solid state quantum chemistry. The main difficulties in trying to obtain a correct description of weakly-bound systems are due to the essential role that dispersive forces play, when covalent and ionic binding is absent, since the long-range forces cannot be correctly described neither by standard Density Functional Theory (DFT) nor Hartree-Fock (HF) approaches. Great efforts in the scientific community to tackle this problem are witnessed by the increasing number of works on this topic in recent literature and different approaches have been proposed.

Post-HF ab initio correlation methods, which are available for molecular calculations since a few years now, have been shown to be able to describe the interaction between molecules in a correct and reliable way. Thanks to the adoption of local methods the relative cost of the calculation is not prohibitive. Despite the potential interest the availability of such methods for crystalline systems is still rather scarce.

In this talk results will be presented concerning the periodic Local Møller Plesset second order perturbation theory (LMP2) method applied to the study of molecular crystals. All calculations are performed using the well known CRYSTAL code and the new CRYSCOR code, the first publicly available program to implement local correlation methods for crystalline systems, which are both developed in our research groups.

Different aspects of the electronic structure simulation of molecular crystals will be covered, including evaluation of cohesive energies and relative stability of different structures as well as properties like Compton profiles and bulk moduli. Results concerning Ice, Carbon dioxide, Urotropine, Urea and Formic acid crystals will be presented and discussed among others.

In addition, the local method allows us to analyze the correlation contribution to the cohesive energy by separating the intramolecular and intermolecular contribution,[4] allowing for an interesting insight on the role of weak interactions in the studied systems. In this respect, crystalline Formic acid is analyzed in more detail.

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Keywords: ab initio, computer simulation, molecular crystals

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Crystal structure prediction of molecular compounds with d-DFT. Jacco van de Streek, Marcus A. Neumann. *Avant-garde Materials Simulation, Freiburg, Germany.*
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The talk will focus on the crystal structure prediction of molecular compounds with dispersion-corrected Density Functional Theory (d-DFT) calculations¹. d-DFT was successfully used to predict all four crystal structures of the 2007 Crystal Structure Prediction Blind Test correctly². This success has meanwhile been extended to larger molecules, to more flexible molecules and to molecular salts. The calculations are carried out with the computer software *GRACE* (<http://www.avmatsim.eu>), which uses the computer software *VASP*³⁻⁵ for single-point uncorrected DFT calculations. An outline of the crystal structure prediction procedure will be given. Results on Efavirenz, Pyridine, Benzamide, Pyridinium Chloride and several Crystal Structure Prediction Blind Test compounds will be presented. Preliminary results for the 2010 Crystal Structure Prediction Blind Test will be included where possible.

[1] Neumann, M. A. & Perrin, M.-A., *J. Phys. Chem. B*, 2005, 109, 15531. [2] Day, G. M., *et al.*, *Acta Cryst. B*, 2009, 65, 107. [3] Kresse, G. & Furthmüller, J., *Phys. Rev. B*, 1996, 54, 11169. [4] Kresse, G. & Hafner, J., *Phys. Rev. B*, 1993, 47, 558. [5] Kresse, G. & Joubert, D., *Phys. Rev. B*, 1999, 59, 1758.

Keywords: crystal structure prediction, dispersion-corrected density functional theory

FA4-MS28-T03

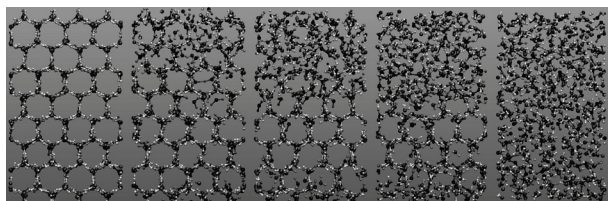
Temperature and Pressure in Computational Crystallography: A Case Study of Ice. Detlef W. M. Hofmann, Marco Cogoni, Liudmila N. Kuleshova, Bruno D'Aguanno *CRS4, Pula, Italy.*
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A notorious problem of computational crystallography are temperature and pressure. The importance of these factors in crystallography becomes obvious by the widespread polymorphism. Here we present molecular dynamic simulations as an alternative to effective potentials with intrinsic temperature and pressure effects. An excellent test case is ice, since it is very well investigated and 15 different crystal structures are known. Proton transfer, diffusion, and proton order/disorder in the ice crystals are studied.

In the last blind test it was shown that effective potentials can be used to predict correctly crystal structures at standard conditions. These requires potentials corrected for the entropy at standard conditions. Earlier we obtain such potentials by data mining on the Cambridge structure data base [1, 2]. Another very successful approach was the dispersion-corrected density functional theory introduced by M. A. Neumann, F. J. J. Leusen, and J. Kendrick.

Another possibility is molecular dynamics. Molecular dynamics gives, in addition to structural properties, access to thermodynamical properties as the entropy, diffusion, proton exchange rates, and conductivity. This method became accessible by the extended computer power available nowadays. For our simulations we used a cluster of 1600 nodes with a total performance of 36 TeraFLOPS.

We performed MD simulations at different conditions for all known structures of ice. As force field we used the reactive force field [3], which allows for proton exchange by bond breaking/formation. The reactive force field was recently derived from neutron scattering by recursive fitting. The simulations reproduce well the melting and boiling point. On the figure five snapshots of our video of the melting are shown.



After equilibration the obtained structures are analyzed by clustering [2, 4]. It allows us to visualize the relationship between the idealized crystal structures and the obtained crystal structures in a classification tree. In dependence of the conditions we observe structural changes in the different polymorphs in accordance with the experimental phase diagram. At high pressure we find the structures VII and VIII stable, at low pressure ice I.

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Keywords: molecular dynamics, reactive force field, cluster analysis

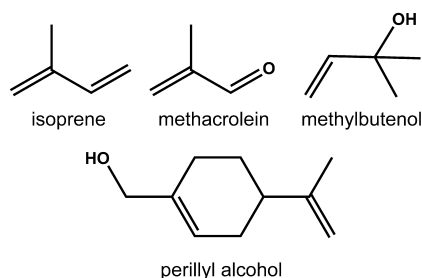
FA4-MS28-T04

Simulation of the interaction of terpenes and their oxidation products with ice. Sonja M. Hammer^a, Christian Czech^a, Boris Bonn^b, Martin U. Schmidt^a.

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Local structures and energies are calculated for the interactions of atmospherically relevant volatile organic compounds (isoprene, methacrolein, methylbutenol, perillyl alcohol) with ice I_h by force-field methods.



Ice I_h is the stable ice polymorph at atmospheric conditions.^[1] When ice (snow/hail/graupel) begins to form in the troposphere, volatile organic compounds will be adsorbed at the surface or incorporated into the crystals.

For all compounds, the interactions were calculated for an adsorption at the (0001) surface of ice as well as for an absorption into the ice bulk as point defect. For methacrolein the interaction with a small-angle grain boundary as a 2D-lattice defect was also considered. For all calculations a modified Dreiding force field was used.^[2] Results:^[3]

For all investigated compounds the adsorption on the (0001) surface is energetically preferred (enthalpies between -15 and -56 kJ mol⁻¹). The adsorption of isoprene at the ice surface is based on van der Waals interactions only. The methacrolein molecule forms two hydrogen bonds with water molecules of the ice surface. The alcohols could either be adsorbed on top of the surface, or, with similar adsorption enthalpies, be incorporated into the surface (replacing one water molecule). In all cases the alcohols form three hydrogen bonds between the OH-group and the water molecules of the ice surface. The absorption into the ice crystal is energetically unfavourable for all compounds. The fraction of adsorbed molecules is calculated with Boltzmann statistic. All molecules are mainly adsorbed on the surface. Only methylbutenol is also incorporated into the ice crystals in significant amounts.

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Keywords: force field method, ice, terpenes

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Experimental and Computational Study of (E)-4-Methyl-2-[[tris(hydroxymethyl)-methyl]iminomethyl]phenolate. Gonca Özdemir Tari^a, Hasan Tanak^a, Mustafa Macit^c, Ferda Erşahin^b, Şamil Işık^a. ^aDepartment of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, Kurupelit, 55139 Samsun, Turkey, ^bGerze Sinop Vocational School, Sinop University, Sinop, Turkey, ^cDepartment of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, Kurupelit, 55139 Samsun, Turkey.

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Schiff bases can be classified by their photochromic and thermochromic properties [Cohen et al., 1964]. In general, Schiff bases based on salicylic aldehyde display two possible tautomeric forms, the iminomethyl-phenol (OH) and the aminomethylene-cyclohexa-2,4-dienone (NH) forms. Depending on the tautomers, two types of intramolecular hydrogen bonds are observed in Schiff bases: O—H···N in the former and N—H···O in the latter tautomer. Another form of the Schiff base compounds is also regarded to be zwitterionic showing an ionic intramolecular hydrogen bond (N⁺—H···O⁻) and this form is rarely seen in the solid state. The NH form of Schiff bases in the solid state can be regarded as a resonance hybrid of two canonical structures, the aminomethylene-cyclohexa-2,4-dienone and the zwitterionic form [Ogawa, *et al.*, 2003].

The crystal and molecular structure of the title compound, C₁₂H₁₇NO₄, has been synthesized and x-ray single-crystal structure determination has been performed. The title molecule exists in a zwitterionic form with a strong intramolecular N⁺—H···O⁻ hydrogen bond between the NH⁺ and the phenolate O⁻. In the crystal structure, molecules are linked together by intermolecular C—H···O and O—H···O interactions

Geometric optimization based on x-ray diffraction technique and quantum mechanical calculations were performed. The calculated geometric parameters were compared to the