smr2054

Structure and Dynamics of Hydrogen-Bonded Systems
(26 - 27 October 2009)

(Miramare, Trieste - Italy)

co-sponsored by:
Centre for Molecular Structure and Dynamics, STFC, U.K.

ORGANIZERS:

J. KOHANOFF   Queen's University, Belfast, U.K.

S. KOVAL   IFIR, University of Rosario, Argentina

R. SENESI   University of Rome Tor Vergata, Italy

LOCAL ORGANIZER:

E. TOSATTI   ICTP-SISSA-DEMOCRITOS
                               Trieste, Italy

BOOK OF ABSTRACTS

web-page: http://agenda.ictp.trieste.it/smr.php?2054

CONTENTS

PREFACE

Hydrogen-bonding is ubiquitous in physical, chemical, and biological sciences. At the root of the unique properties of water and of polymorphism in ices and in organic crystals, it is also involved in most biochemical processes such as enzyme catalysis. Protons and deuterons in hydrogen bonds behave as quantum-mechanical particles and, as such, they give rise to a variety of interesting quantum phenomena such as tunneling and geometric effects. Recent advances in neutron and X-ray scattering provide the tools for the accurate determination of the structure and dynamics of protons in hydrogen bonds. For example, deep inelastic neutron scattering recently showed, for the first time, direct evidence of proton tunneling in KDP. Parallel to that, advances in computational techniques such as path integral and wave function methods have allowed for the introduction of quantum nuclear effects on the theory of structural and dynamical properties of these systems. Classical and quantum molecular dynamics methodologies are frequently used as a complementary tool to the experimental ones. The coming together of all these elements makes this an extremely exciting time for the field, a time when substantial advances in our understanding of hydrogen bonded systems appear possible. The focus of this meeting will be on cutting-edge experimental and computational approaches, and on recent results aiming at describing and understanding the peculiarities of hydrogen-bonded systems in condensed phases such as solids, liquids, and macromolecular systems.

We acknowledge and give thanks to our co-sponsors Centre for Molecular Structure and Dynamics, STFC, U.K., for their kind contribution towards this event.

The Organizers wish you a most exciting and enjoyable meeting.
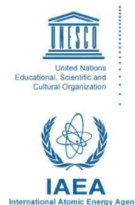

Jorge Kohanoff   Erio Tosatti
Sergio Koval   Doreen Sauleek
Roberto Senesi

PROGRAMME

(as of 20 October 2009)

The Abdus Salam
International Centre for Theoretical Physics

Structure and Dynamics of Hydrogen-Bonded Systems

Cosponsor(s): co-sponsored by: Centre for Molecular Structure and Dynamics, STFC, UK
Organizer(s): Directors: J. Kohanoff, S. Koval, R. Senesi Local Organizer: E. Tosatti
Trieste - Italy, 26 - 27 October 2009

Venue: Leonardo da Vinci Building Main Lecture Hall

Preliminary Programme

MONDAY, 26 OCTOBER 2009 (Room:Leonardo da Vinci Building Main Lecture Hall)

26 October 2009

08:30 - 09:00   (Room: Leonardo da Vinci Building, Lobby)
                --- REGISTRATION & ADMINISTRATIVE FORMALITIES ---

09:00 - 09:05   **OPENING SESSION**

Session 1 - ICE AND ITS SURFACE (in honor of Victoria Buch) (Room:Leonardo da Vinci Building Main Lecture Hall)

26 October 2009

09:00 - 09:25   **Erio TOSATTI** / *SISSA, ICTP & CNR/INFM Democritos, Trieste, Italy*
                Ice and Victoria Buch: a cold surface and a warm heart

09:25 - 09:50   **Thomas KUEHNE** / *Harvard University, Cambridge, U.S.A.*
                The aqueous liquid-vapor interface: new insights from a novel Car-Parrinello-like approach to Born-Oppenheimer molecular dynamics

09:50 - 10:15   **Olivia PULCI** / *Universita' di Roma II "Tor Vergata", Italy*
                Effect of proton disorder in the excited state properties of ice

10:15 - 10:40   **Livia BOVE** / *Universite' Pierre et Marie Curie Paris VI, Paris, France*
                Concerted proton tunnelling in ordinary ice

10:40 - 11:10   (Room: Leonardo da Vinci Building, Lobby)
                     --- COFFEE BREAK ---

SESSION 2 - LIQUIDS (Room:Leonardo da Vinci Building Main Lecture Hall)

26 October 2009

11:10 - 11:50   **Alan SOPER** / *Rutherford Appleton Laboratory, Didcot, U.K.*
                     Is ambient water homogeneous of inhomogeneous?

11:50 - 12:30   **Tristan YOUNGS** / *The Queen's University of Belfast, U.K.*
                     **Molecular solvents over heterogeneous surfaces and ionic liquids in the bulk - experimental and
                     theoretical study of hydrogen bonding systems**

12:30 - 14:00   (Room: Leonardo da Vinci Building Cafeteria)
                     --- LUNCH BREAK ---

14:00 - 14:40   **Carla ANDREANI** / *Universita' di Roma II "Tor Vergata", Italy*
                     Proton quantum effects in water

14:40 - 15:20   **Joseph MORRONE** / *Columbia University, New York, U.S.A.*
                     Nuclear quantum effects in water: a study in position and momentum space

15:20 - 16:00   **David MANOLOPOULOS** / *University of Oxford, U.K.*
                     Competing quantum effects in liquid water

16:00 - 16:30   (Room: Leonardo da Vinci Building, Lobby)
                     --- COFFEE BREAK ---

16:30 - 17:10   **Ruth LYNDEN-BELL** / *University of Cambridge, U.K.*
                     Simulations of water and artificial liquids with weakened hydrogen bonds

17:10 - 17:50   **Chick WILSON** / *University of Glasgow, U.K.*
                     **The evolution of hydrogen bonds in molecular materials under changing external conditions by
                     neutron diffraction and complementary methods**

17:50 - 18:30   --- BREAK & REFRESHMENTS ---

18:30 - 20:00   **POSTER SESSION**
                     Poster Gallery (behind the Main Lecture Hall)

20:00 - 23:00   --- SOCIAL DINNER ---

TUESDAY, 27 OCTOBER 2008 (Room:Leonardo da Vinci Building Main Lecture Hall)

27 October 2009

08:30 - 09:00   (Room: Leonardo da Vinci Building, Lobby)
                     --- REGISTRATION & ADMINISTRATIVE FORMALITIES ---

SESSION 3 - SOLIDS (Room:Leonardo da Vinci Building Main Lecture Hall)

27 October 2009

09:00 - 09:30   **Biswajit SANTRA** / *FHI der Max-Planck-Gesellschaft, Berlin, Germany*
On the accuracy of density-functional theory exchange-correlation functionals for hydrogen bonds in water

09:30 - 09:50   **Jorge KOHANOFF** / *The Queen's University of Belfast, U.K.*
Quantization of vibrations in H-bonded crystals

09:50 - 10:20   **Keith REFSON** / *Rutherford Appleton Laboratory, Didcot, U.K.*
Strong anharmonicity and isotope effects in Cr00H/Cr00D

10:20 - 10:40   **Sergio KOVAL** / *Universidad Nacional de Rosario, Argentina*
H-bonded Ferroelectrics from first-principles and derived modeling

10:40 - 11:00   (Room: Leonardo da Vinci Building, Lobby)
--- COFFEE BREAK ---

11:00 - 11:30   **John LOVEDAY** / *University of Edinburgh, U.K.*
High pressure structural studies of hydrogen bond centring

11:30 - 12:00   **Mark JOHNSON** / *Institut Max Von Laue-Paul Langevin, Grenoble, France*
Proton dynamics in short hydrogen bonds: two-site hopping in a single-well potential

---

SESSION 4 - LIQUID/SOLID INTERFACES (Room:Leonardo da Vinci Building Main Lecture Hall)
27 October 2009

12:00 - 12:30   **Pepa CABRERA-SANFELIX** / *Donostia International Physics Center, San Sebastian, Spain*
Water adsorption on 0/Ru(0001): Dissociation and cooperative effects

12:30 - 13:00   **Angelos MICHAELIDES** / *University College London, U.K.*
The quantum nature of the proton in water-hydroxyl overlayers on metal surfaces

13:00 - 14:00   (Room: Leonardo da Vinci Building Cafeteria)
--- LUNCH BREAK ---

SESSION 5 - CHEMISTRY/BIOLOGICAL SYSTEMS (Room:Leonardo da Vinci Building Main Lecture Hall)
27 October 2009

14:00 - 14:40   **Martina HAVENITH** / *Ruhr-Universitaet Bochum, Germany*
Chemistry below 1 K: Observation of the smallest droplet of acid

14:40 - 15:10   **Mariana ROSSI** / *FHI der Max-Planck-Gesellschaft, Berlin, Germany*
Secondary structure of H-bonded Polyalanine peptides in vacuo: Computational spectroscopy and DFT

15:10 - 15:50   **Raul CACHAU** / *National Cancer Instiute, Frederick, U.S.A.*
Study of mobile protons in enzymes as revealed by subatomic x-ray and neutron diffraction experiments

15:50 - 16:30   **Janez MAVRI** / *National Institute of Chemistry, Ljubljana, Slovenia*
Dynamics of proton transfer in biological systems

16:30 - 16:50   **Roberto SENESI** / *II Universita' di Roma "Tor Vergata", Italy*
Proton momentum distribution of water confined in nanopores, protein hydration shells and DNA

16:50 - 17:20   (Room: Leonardo da Vinci Building, Lobby)
                           --- COFFEE BREAK ---

SESSION 6 - CONFINED SYSTEMS (Room:Leonardo da Vinci Building Main Lecture Hall)

27 October 2009

17:20 - 18:00   **Christiane ALBA-SIMIONESCO** / *CEA Saclay, Gif-sur-Yvette, France*
                           Melting and glass formation in some nano-confined H-bonded liquids

18:00 - 18:30   **Jonas BJOERK** / *University of Liverpool, U.K.*
                           Hydrogen-bonding in bi-component supramolecular nanoporous networks

18:30 - 18:45   **CLOSING SESSION**

ABSTRACTS

OF

INVITED TALKS

(in order of presentation, as per programme updated 20 October 2009)

Ice and Victoria Buch: a cold surface and a warm heart

Erio Tosatti
SISSA, ICTP, and CNR/INFM Democritos, Trieste, Italy

Victoria Buch, who knew so much about ice and hydrogen bonds, was intrigued and fascinated by the possible physical states of the ice surface. She knew on one hand that it was only reasonable to expect the proton disorder of bulk ice to persist at the surface. She also on the other hand felt, or hoped, that the surface energetics should favor some new type of surface proton order, absent in bulk ice.

To pursue this fragile dream, she stole time away from her heartier physico-chemical studies, and from her warm-hearted generous political battles within Israel, to collaborate with a surface theorist, whom she met by chance one summer in Lugano -- me. Me, who would contribute nothing more than some generic wisdom, and no actual hard calculations.

Her own calculations, both Molecular Dynamics and Monte Carlo, eventually showed that in the cold ice surface not only the oxygen atoms would stay put and crystalline up until some 180 K, but showed that at low enough temperatures the protons too would order -- and that in spite of proton disorder in the underlying bulk! My own job ended up being to recognize that this surface order, 2x1 stripes formed by rows of "dangling hydrogens" and "dangling oxygens" (an old suggestion by Fletcher) could finally make sense of some unexplained helium scattering data obtained a decade earlier in Goettingen.

Victoria and I were still collaborating, and spending hours on the phone at that, when her fatal disease came. She very much wanted to find out how fragile or robust the ordered surface striped phase would be against temperature. My Landay theory said there should be a first order transition between 2x1 stripes and thermal disorder, at some unknown temperature. Her preliminary model Monte Carlo study found precisely such a transition around 60 K. While we must now wait for some data or for newer, less tentative calculations to follow those by Victoria, 60 K remains my best estimate for the "Buch transition" temperature at the surface of hexagonal ice.

The Aqueous Liquid-Vapor Interface: New Insights from a Novel Car-Parrinello-like Approach to Born-Oppenheimer Molecular Dynamics

Thomas D. Kühne[1] and Yousung Jung[2]

[1] *Department of Physics and School of Engineering & Applied Sciences, Harvard University, Cambridge, MA 02138, USA*

[2] *Graduate School of EEWS, KAIST, Yuseong-gu, Daejeon 305-701, Korea*

Surface and interface properties of liquid water are of crucial importance for various processes in biology, chemistry and atmospheric sciences. However, studying the water surface is rather challenging due to the required system size to stabilize the surface, the 2D periodic boundary conditions and the hence reduced statistics in comparison to the bulk. Nevertheless, using the recently devised Car-Parrinello-like approach to Born-Oppenheimer molecular dynamics [1] it became now possible to study the aqueous liquid-water interface from first principles with great accuracy.

Applying a new hydrogen-bond definition [2], based on two-dimensional potentials of mean force, we find substantially less single-donor and acceptor-only moieties as in the groundbreaking study of Kuo and Mundy [3], but in good agreement with recent sum frequency generation experiments. Studying the orientational distribution of the water molecules near the surface we find that dangling OH bonds and lone pairs are not equally distributed, but that the dangling bonds are preferably protruding out of the water interface, while the lone pairs tend to point into the water phase. This leads to an asymmetry of the hydrogen-bond network near the surface, as can be seen by means of the spatial distribution function, and a shortening of the intramolecular OH bond lengths.

References

[1] T. D. Kühne, M. Krack, F. Mohamed and M. Parrinello, Phys. Rev. Lett. **98**, 066401 (2007); T. D. Kühne and M. Parrinello (in preparation)

[2] R. Kumar, J. R. Schmidt and J. L. Skinner, J. Chem. Phys. **126**, 204107 (2007).

[3] I.-F. W. Kuo and C. J. Mundy, Science **303**, 658 (2004).

Effect of proton disorder in the excited state properties of ice

Viviana Garbuio (1), Rodolfo Del Sole (1), and Olivia Pulci (1)

(1) ETSF and Tor Vergata university and CNR-INFM, Roma

Ordinary ice has a hexagonal crystal structure (ice Ih). A metastable cubic crystalline variant of ice exists, where oxygen atoms are arranged in a diamond structure (ice Ic), and the hydrogen ones are disordered, still obeying the Pauling ice rules. It is produced at temperatures between 130-150 K, and is stable for up to 200 K, when it transforms into ice Ih. The proton disorder in ice has a role in several properties such as growth condition and thermal properties [1,2] and many works about phase transitions from proton disordered to proton ordered ices can be found in literature. Moreover, depending on the proton ordering, some ice phases can also present ferroelectric or antiferroelectric behaviors [3,4].

In recent years, the excited state properties of hexagonal ice have been studied within many-body perturbation theory (MBPT) [5]. The electronic and optical properties of cubic ice, instead, have never been calculated accurately: only tight-binding [6,7] and density functional theory (DFT) [8,9] calculations have appeared in the literature. Moreover, in several of these studies the proton disorder is not taken into consideration. Here, we present MBPT calculations of the electronic and optical properties of cubic ice exploiting model cells with different level of proton disorder and we compare our results with ice Ih and with liquid water.

Preliminary results on ice surfaces are also discussed.

[1] G. P. Johari et al., J. Chem. Phys. 122, 194504 (2005)
[2] G. P. Johari et al., Chem. Phys. 258, 277 (2000)
[3] V. Buch et al., J. Phys. Chem. B 44, 8641 (1998)
[4] J. Lekner, Physica B: Cond. Matter 252, 149 (1998)
[5] P. H. Hahn et al., Phys. Rev. Lett. 94, 037404 (2005)
[6] G. Pastori Parravicini et al., Phys. Rev. B 8, 1973 (1973)
[7] L. Resca et al., phys. stat. sol. b 81, 129 (1977)
[8] W. Y. Ching et al., Phys. Rev. Lett. 71, 2840 (1993)
[9] W. Y. Ching et al., Ferroelectrics 153, 25 (1994)

Concerted proton tunnelling in ordinary ice

L.E. Bove[1], S. Klotz[1], A. Paciaroni[2], F. Sacchetti[2]

[1] *IMPMC, CNRS- Université P. et M. Curie, F-75252 Paris, France.*
[2] *CNR-INFM CRS-Soft, c/o Dipartimento di Fisica, Università di Perugia,
I-06123 Perugia, Italy.*

We present high-resolution, incoherent quasielastic neutron scattering measurements on ice Ih (ordinary ice) and Ic (cubic ice) which show the existence of an anomalous, non-harmonic motion of hydrogen at low temperatures. We show that this dynamics is localized, non-vibrational, and related to the hydrogen disorder since it is absent in the hydrogen-ordered phase, ice VIII (see figure). A main jump distance of 0.75 Angstrom is identified, i.e. close to the distance between the two possible proton sites along the oxygen-oxygen bond. The motion is non-Arhenius, has a large time rate of 2.7×10^{11} s^{-1}, and affects only a few percent of the total number of hydrogen atoms in the crystal [1]. A partial (20%) deuteration of the sample, assuring, statistically, a breaking of the symmetry of the *ordered hexagonal rings* [2], hinders the observed dynamics.

These results give evidence for the existence of concerted proton tunnelling in these ice phases.

[1] L.E. Bove et al., Phys. Rev. Lett., in press October 2009.
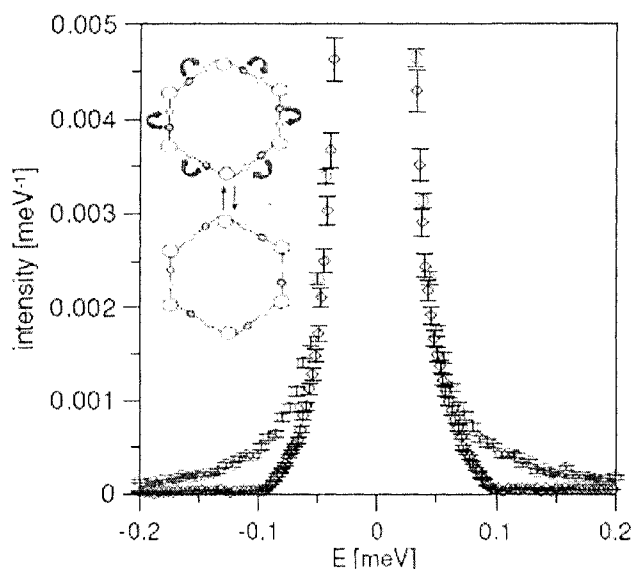[2] L. Pauling, J. Am. Chem Soc. 57, 2680, 1935.

Figure 1: Quasi-elastic contribution in ice Ih (red circles) compared with ice VIII (blue rhombus) at 5 K. The ice VIII spectrum is coincident with the measured instrument energy resolution. Insert: a sketch of the proposed concerted tunnelling of the hydrogen atoms in the *hexagonal ordered loops*.

Is ambient water homogeneous or inhomogeneous?

Alan K. Soper
ISIS Facility,
STFC Rutherford Appleton Laboratory,
Harwell Science and Innovation Campus,
Didcot, Oxon OX11 0QX, UK

In a recent paper (PNAS, 2009, vol. 106, p.15214-15218) it is claimed structural heterogeneities have been observed in ambient water, based on small angle x-ray scattering (SAXS) and x-ray absorption and emission spectroscopies (XAS,XES). The evidence for this comes from two sources, namely the (small) rise in scattering at low wave vectors (Q) that occurs in the SAXS pattern for water, and the shapes of the XAS and XES spectra and the behaviour of these spectra with changing temperature. Using neutron and x-ray diffraction data and combining these with empirical potential structure refinement (EPSR) simulations, it is shown here that these claims are misconstrued, depending rather delicately on what exactly is meant by "inhomogeneous". The density fluctuations in water in the temperature range 0 - 100C are shown to have a single mode, do not exhibit the two (or more) mode structure that might be implied by the inhomogeneous model, and are more than sufficient to explain the low Q rise in the small angle x-ray scattering.It is also shown that current interpretations of XAS data from water using theoretical techniques are highly variable, and an alternative, evidence based, interpretation is proposed.

"Molecular solvents over heterogeneous surfaces and ionic liquids in the bulk - experimental and theoretical study of hydrogen bonding systems"

Dr. T. Youngs
(t.youngs@qub.ac.uk)

Atomistic Simulation Centre
Old Physics Building
Queen's University Belfast
Belfast, BT7 1NN, N.I.
U.K.

Ionic liquids represent an interesting class of solvents for structural studies to focus upon, even if their potential practical uses are occasionally over-hyped. The presence of hydrogen bonding in the liquid state is now well accepted and, in the context of experimental structural studies, adds another subtlety by which to challenge any data refinement procedures. An overview of hydrogen bonding in ionic liquids is provided, the resulting effects on the liquid state are discussed, and recent neutron diffraction data and its refinement on specific ionic liquid systems is presented and discussed.

On an entirely different note, the underlying oxide supports used in heterogeneous catalysis are often considered the prevalent influence on the structure of hydrogen bonding molecular solvents. Simulation studies of partially hydroxylated surfaces have shown, however, that surface heterogeneities can have a significant effect on the structure also. Molecular dynamics simulations of thin films over model ionic surfaces containing 'catalyst' patches will be presented, extending the idea of liquid structuring arising from such inhomogeneities on the surface.

Proton quantum effects in water

Carla Andreani

Università degli Studi di Roma Tor Vergata,
Dipartimento di Fisica and Centro NAST,
Via Ricerca Scientifica 1, 00133 Rome, Italy

ABSTRACT

Proton quantum effects, for example those associated with the breaking and distortion of hydrogen bonds, are very effectively revealed by measurements of proton momentum distributions, $n(p)$, and mean kinetic energy, $<E_K>$, via Deep Inelastic Neutron Scattering (DINS). DINS investigations complement x-ray and neutron studies on spatial distributions of the proton. Both physical quantities $n(p)$ and $<E_K>$ provide unique information on the "effective potential" that the proton sees as the hydrogen bond network changes, as for instance in presence of proton tunneling, delocalization and breaking of H bonding. Due to the quantum mechanical non commuting property of position and momentum, the shape of proton momentum distribution is directly related to the shape of the effective proton potential. Differences in $n(p)$ between liquid water and ice reflect for example the breaking and distortion of hydrogen bonds that occurs upon melting.

In this talk direct DINS measurements of the proton $n(p)$ and $<E_K>$ in stable and supercooled water are presented. Results show a strong temperature dependence of proton $n(p)$ lineshapes and $<E_K>$ in liquid water around the density maximum and in the metastable phase.

Nuclear quantum effects in water: a study in position and momentum space

Joseph Morrone
Columbia University
New York, USA

The importance of nuclear quantum effects in hydrogen bonded systems has been underlined by recent experimental measurements of the proton momentum distribution. In this work, we utilize open path integral Car-Parrinello molecular dynamics simulations in order to compute the proton momentum distribution and assess the impact of nuclear quantum effects in several phases of water. We find that our results are in good agreement with the experimental momentum distributions measured in liquid water and hexagonal ice. It is also found that the inclusion of nuclear quantum effects systematically improves the agreement of first-principles simulations of liquid water with experiment. In addition, we study phases of high-pressure ice that exhibit symmetric hydrogen bonds and quantum tunneling. The symmetric hydrogen bonded phase possesses a narrowed momentum distribution as compared with a covalently bonded phase, in agreement with recent experimental findings. The signatures of tunneling that we observe are a narrowed distribution in the low-to-intermediate momentum region, with a tail that extends to match the result of the covalently bonded state. The transition to tunneling behavior shows similarity to features observed in recent experiments performed on confined water.

Simulations of water and artificial liquids with weakened hydrogen bonds

Ruth M. Lynden-Bell
Department of Chemistry
University of Cambridge
United Kingdom

The effect of hydrogen bonds on the properties of liquid water are investigated by comparing classical simulations of SPC/E liquid water with a family of artificial liquids with reduced hydrogen bond strengths. The effects of the tetrahedral network are studied with a family of artificial models with altered bond angles.

The Evolution of Hydrogen Bonds in Molecular Materials Under Changing External Conditions by Neutron Diffraction and Complementary Methods

Chick C Wilson
Department of Chemistry and WestCHEM Research School,
University of Glasgow, Glasgow G12 8QQ, UK

Much of our recent experimental work has focused on the use of X-ray and neutron diffraction to study the structural evolution of hydrogen bonded molecular systems, including polymorphic materials, molecular complexes, tautomeric molecular materials, systems exhibiting hydrogen atom transfer and disorder, and magnetic systems coupled through hydrogen bond motifs. In particular we have focused on multi-temperature and pressure approaches to these studies, revealing often subtle behaviour of the hydrogen bonding, the structural evolution and on some cases of evolution of physical properties. Some of these effects are sufficiently subtle as to challenge the limits of current experimental diffraction, and also to challenge our theories of hydrogen bond formation.

As a complementary approach to understanding these systems, we have for some years been applying developing plane-wave (periodic) density functional theory calculations for studying hydrogen bonds in the solid state. These are shown to have real potential in the study of a variety of hydrogen bonding systems. In addition MD approaches have been developed for these calculations, which allow us to examine the temperature evolution of molecular structures in the solid state and to quantify proton transfer effects. This leads to a fuller understanding of hydrogen bond formation and offers an improved description of the structural evolution observed in experiments.

These approaches will be illustrated by results from a range of studies including: proton transfer systems, including examples in which the rational design and control of the degree of proton transfer is achieved; materials with potentially cooperative hydrogen bonding; tautomeric hydrogen bonded systems in which very small experimental energy differences can be reproduced and understood; prediction of energy scales for polymorphism in hydrogen-bonded molecular complexes, and optimisation of magnetic coupling in inorganic materials by design of simple hydrogen-bonded linkages.

On the accuracy of density-functional theory exchange-correlation functionals for hydrogen bonds in water

Authors:
Biswajit Santra, Angelos Michaelides and Matthias Scheffler

Abstract:

Despite widespread application of density-functional theory (DFT) to the treatment of water in various environments, for example, liquid water, ice, adsorbed, and confined water, there are still question marks over how well DFT with exchange-correlation (xc) functionals such as PBE and BLYP describe hydrogen bonds between H_2O molecules. Here, we address this issue through a series of studies on water clusters. Such clusters are important in their own right (implicated in phenomena such as acid rain formation and ice nucleation) and, moreover, are amenable to treatment with explicitly correlated quantum chemistry methods and quantum Monte Carlo.

Using coupled cluster with single and double excitations plus a perturbative correction for connected triples [CCSD(T)] as a reference, we have considered how well a range of xc functionals perform in describing the energetics of water monomers and dimers extracted from DFT simulations of liquid water. A key observation is that both PBE and BLYP significantly overestimate the dissociation energies of water dimers extracted from the liquid, in marked contrast to how these functionals perform for water clusters in their equilibrium gas phase geometries. This is because PBE and BLYP incorrectly describe the cost to stretch the OH bonds of the water molecules to their distorted liquid water geometries. Thus we provide a possible explanation for the overstructured radial distribution functions routinely observed in BLYP and PBE simulations of liquid water.

Quantization of vibrations in H-bonded crystals

Jorge Kohanoff
The Queen's University of Belfast
School of Mathematics and Physics
Atomistic Simulation Group
University Road
BT7 1NN Belfast, U.K.

In this talk I will present a general methodology to include the effect of the quantization of vibrations on the structural and dynamical properties of crystals and molecules. The method is based on mapping a suitable subspace of the vibrational manifold and solving the Schroedinger equation in it, in a series of increasingly accurate approximations. I will present results for a model monoatomic chain and a hydrogen-bonded diatomic chain, and analyze them in detail. I will then show results for a more realistic case of a hydrogen-bonded linear F-H chain described at a first-principles level.

The focus is placed specifically on quantum nuclear effects on lattice constants and interatomic parameters.[1] A truly realistic application that solves a long standing question will be presented by K. Refson.

[1] I. Scivetti, N. Gidopoulos, and J. Kohanoff, Phys. Rev. B 78, 224108 (2008)

H-bonded Ferroelectrics from First-Principles and Derived Modeling

Sergio Koval

Instituto de Física Rosario (IFIR), Universidad Nacional de Rosario (UNR), CONICET,
Bv. 27 de Febrero 210 Bis, 2000 Rosario, Argentina.
e-mail: koval@ifir-conicet.gov.ar

Hydrogen bonded ferroelectrics of the KH_2PO_4(KDP)-type family, have attracted much attention in the last decades due to the controversy in the origin of its phase transition and the observed huge isotope effect by deuteration. Experiments like neutron diffraction [1] or Compton scattering [2] as well as diverse models [3] have contributed to shed light in the dispute between tunneling and geometrical effects as the root of the dramatic effect. However the phenomenon has been elusive and the knowledge gained in the last decades is still incomplete. We have tackled this problem in recent years with first-principles calculations in order to unveil some of the microscopic clues responsible of such striking behaviors. In this talk, I will briefly discuss the most important results obtained from first-principles and derived model calculations in two prototypes of these systems: ferroelectric KDP and antiferroelectric $NH_4H_2PO_4$ (ADP). [4-7] I will show that in KDP, tunneling is only possible by means of clusters containing both light and heavy atoms and that the huge isotope effect is a consequence of a self-consistent amplification between tunneling and the geometrical effect in the H-bonds in accordance with experiments [4,5]. The origin of ferroelectricity in KDP is attributed to the proton off-centering, while the stabilization of the antiferroelectric phase in ADP is originated in an optimization of the N-H-O bonds [6]. Finally, I will briefly comment on a first-principles based shell-model which was derived for KDP [7]. This model reproduces phonons, structural and energetic features and will enable us to study the quantum dynamics near the phase transition in large-scale simulations.

[1] R. J. Nelmes, M. I. McMahon, R. O. Piltz, N. G. Wright, , Ferroelectrics **124**, 355 (1991).
[2] G. F. Reiter, J. Mayers and P. Platzman, Phys. Rev. Lett. **89**, 135505 (2002).
[3] R. Blinc, J. Phys. Chem. Solids **13**, 204 (1960); H. Sugimoto and S. Ikeda, Phys. Rev. Lett. **67**, 1306 (1991); D. Merunka and B. Rakvin, Chem. Phys. Lett. **393**, 558 (2004).
[4] S. Koval, J. Kohanoff, R. L. Migoni and E. Tosatti, Phys. Rev. Lett. **89**, 187602 (2002).
[5] S. Koval, J. Kohanoff, J. Lasave, G. Colizzi, and R. L. Migoni, Phys. Rev. B **71**, 184102 (2005).
[6] J. Lasave, S. Koval, N. S. Dalal, and R. L. Migoni, Phys. Rev. Lett. **98**, 267601 (2007).
[7] J. Lasave, J. Kohanoff, R.L. Migoni and S. Koval, Physica B **404**, 2736 (2009).

High Pressure Structural Studies of Hydrogen Bond Centring

J.S. Loveday, R.J. Nelmes, C.L. Bull, M. Guthrie, K. Komatsu and H. Hamidov

SUPA, School of Physics and Astronomy and Centre for Science at Extreme Conditions, The University of Edinburgh, Edinburgh, United Kingdom.

Pressure provides a powerful means to explore the effects of H-bond centring. Easily available pressures can make large changes in H-bond geometry, allowing studies of H-bonds under a wide range of strengths. In addition, pressure makes these geometric changes cleanly by varying the density without the complications introduced by chemical substitution when geometry changes are made by "chemical pressure". As a result, ice, one of the simplest H-bonded systems, has been intensively studied. Here, the aim has been to observe the transition to centred ice X, where the proton reaches the centre of the hydrogen bond. Raman and infra-red studies report the onset of the transition at ~70 GPa, but find that the transition is not complete until ~120 GPa [1]. Ab-initio molecular dynamics studies support this view and find evidence of quantum smearing of the protons over a pressure range of ~50 GPa around the centring transition [2].

Direct structural information on the proton distributions in this pressure range would greatly improve our understanding of the centring transition in ice. However, the pressures involved remain much too high at present for neutron diffraction which is the only technique able to make such measurements. H-bonded ferroelectrics such as potassium dihydrogen phosphate (KDP), potassium dideuterium phosphate (DKDP) and squaric acid ($H_2C_4O_4$, H_2SQ) provide more tractable analogues for structural studies of H-bond centring. Their structures have been studied in detail at ambient pressure and up to ~2 GPa by high resolution neutron diffraction [3], and are estimated to undergo hydrogen-bond centring at pressures between 5 and 10 GPa [3]. Recent developments to the Paris-Edinburgh cell have now extended the maximum pressure for single-crystal neutron diffraction studies to 10 GPa and hence make it possible to determine structures at pressures close to the centring transition.

We will present the results of neutron diffraction studies of KDP, DKDP and H_2SQ up to 10 GPa. These studies reveal that the proton/deuteron distributions remain strongly elongated at pressures where the H-bond appears to be centred.

[1] A.F. Goncharov, V.V. Struzhkin, M.S. Somayazulu, R.J. Hemley and H.K. Mao, Science **272**, 218-220 (1996)
[2] M. Benoit, D. Marx and M. Parinello, Nature **392**, 258-261 (1998).
[3] Z. Tun, R.J. Nelmes and G.J. McIntyre, J. Phys. C **20**, 5667-5675 (1987) and M.I. McMahon, R.O. Piltz and R.J. Nelmes, Ferroelectrics **108**, 277-282 (1990).

PROTON DYNAMICS IN SHORT HYDROGEN BONDS: TWO-SITE HOPPING IN A SINGLE-WELL POTENTIAL.

M.R. Johnson, H.P. Trommsdorff, A. Ivanov
(Institut Laue Langevin, Grenoble, France)

I.R. Evans, S.J. Ford
(Department of Chemistry, University of Durham, Durham, UK)

A.J. Horsewill, I. Frantsurov
(School of Physics & Astronomy, University of Nottingham, Nottingham, UK)

ëNormalí hydrogen bonds are characterised by a two-well, potential energy surface (PES) in which the proton can jump from one well to the other [1]. In contrast, short hydrogen bonds are characterised by a single, potential energy well for the proton which, at first sight, would seem to limit the proton dynamics to small amplitude vibrations. Crystallographic measurements reveal however a proton migration effect with increasing temperature in some short hydrogen bonds [2, 3]. Furthermore, short hydrogen bonds are thought to play a key role in important chemical and bio-physical processes (e.g. enzyme catalysis [4]), which would be difficult to understand in terms of a static, albeit anharmonic, single-well potential.

The crystallographic data has been understood with the aid of ab initio molecular dynamics simulations [5,6] which show that fluctuations in the potential energy well, driven by lattice phonons, are responsible for proton migration. In fact, the time-averaged potential energy surface has two minima, resembling the PES of the normal hydrogen bond, and the proton dynamics underlying proton migration can effectively be viewed as two-site hopping, as for a normal hydrogen bond. In order to confirm this model of proton dynamics, two-site hopping in a single-well potential, we have recently undertaken a series of experiments including quasielastic neutron scattering, vibrational spectroscopy and field-cycling NMR.

We will present an overview of the computational results for 3,5-pyridine dicarboxylic acid followed by new experimental evidence for proton hopping in the fluctuating, single-well potential of the short hydrogen bond and the role of entropy on the proton dynamics. A new, more detailed crystallographic study will be presented on a poster.

[1] Neumann; Brougham; McGloin; Johnson; Horsewill; Trommsdorff; J.Chem.Phys. 109 (1997) 7300
[2] Wilson; Acta.Cryst. 2001, B57, 435-439
[3] Cowan, Howard, McIntyre, Lo, Williams; Acta.Cryst.B61 (2005) 724S.M.-F.
[4] e.g. Cleland, Kreevoy; Science 264 (1994), 1887
[5] Fontaine-Vive, Johnson, Kearley, Howard, Parker; J.Am.Chem.Soc. 128 (2006) 2963 & Morrison, Siddick, Camp, Wilson; J.Am.Chem.Soc, 127 (2005) 4042
[6] Fontaine-Vive, Johnson, Kearley, Cowan, Howard, Parker; J. Chem. Phys. 24 (2006) 234503

Water Adsorption on O/Ru(0001): Dissociation and Cooperative Effects

Pepa Cabrera-Sanfelix,[1] Andrés Arnau,[2,3] Aitor Mugarza,[4] Tomoko K. Shimizu,[5,6] Miquel Salmeron[5,6] and Daniel Sánchez-Portal[2]

[1] Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, San Sebastian 20018, Spain. swbcasam@sc.ehu.es
[2] Unidad de Física de Materiales, Centro Mixto CSIC-UPV, Apdo. 1072, San Sebastián 20080, Spain
[3] Departamento de Física de Materiales UPV/EHU, Facultad de Química, Apdo. 1072, San Sebastián 20080, Spain
[4] Institut de Ciencia de Materials de Barcelona, CSIC, Bellaterra 08193, Spain
[5] Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
[6] Department of Materials Science and Engineering, University of California, Berkeley, CA 94720, USA

Using density functional theory we found that, depending on coverage, co-adsorbed oxygen can act both as a promoter and as an inhibitor of the dissociation of water on Ru(0001), the transition between these two behaviours occurring at ~0.2 ML. The factors determining this transition are (i) hydrogen bond between $H_2O - O_{ads}$ and (ii) the adsorption energy of the reaction products, OH in particular (see Table 1). The chemistry of this co-adsorbed system is dictated by the effective coordination of the Ru atoms that participate in the bonding of the different species. In particular, we observed that a low coverage of oxygen increases the adsorption energy of the OH fraction on the Ru surface. This surprising extra-stabilization of the OH with the co-adsorption of oxygen can be understood in the context of the metallic bonding and could well correspond to a general trend for the co-adsorption of electronegative species on metallic surfaces.[1] On the other hand, the cooperative adsorption of water on the metallic substrate reinforces significantly the intermolecular interaction. Here, we present a molecular-scale description of the dimer hydrogen bond strengthen induced by the formation of a bond between the donor water molecule and the Ru substrate. This strong hydrogen bond involves the weakening of the intramolecular OH bond of the donor molecule, which might facilitate the partial dissociation of water.[2]

Table I. Adsorption energies (Eads) of H, OH and H2O adsorbed on Ru(0001) at different θO. The energy gained by dissociative adsorption, , defined by = + − ; where = 5.58 eV is the required energy for partial dissociation of the water molecule in vacuum. The relative stability of dissociative versus molecular adsorption, ΔE, is defined by ΔE = − . Notice that positive values of ΔE denote favoured dissociative over intact adsorption.

Surface	E_{ads}^{H} (eV)	E_{ads}^{OH} (eV)	$E_{ads}^{H_2O}$ (meV)	$E_{diss}^{H_2O}$ (meV)	ΔE (meV)
Ru(0001)	2.90 (fcc)	3.49 (fcc/hcp)	474	821	347
O(4x4)/ Ru(0001)	2.89 (fcc)	3.61 (hcp/fcc)	533	925	392
O(2x4)/ Ru(0001)	2.86 (fcc)	3.64 (hcp)	612	920	308
O(2x2)/ Ru(0001)	2.60 (fcc)	3.10 (top/hcp)	616	127	-489

Ru(0001)

E_{H_2O} = - 474meV E_{H+OH} = - 821meV

O(4x4)/Ru(0001)

E_{H_2O} = - 533meV E_{H+OH} = - 925meV

O(2x4)/Ru(0001)

E_{H_2O} = - 612meV E_{H+OH} = - 920meV

O(2x2)/Ru(0001)

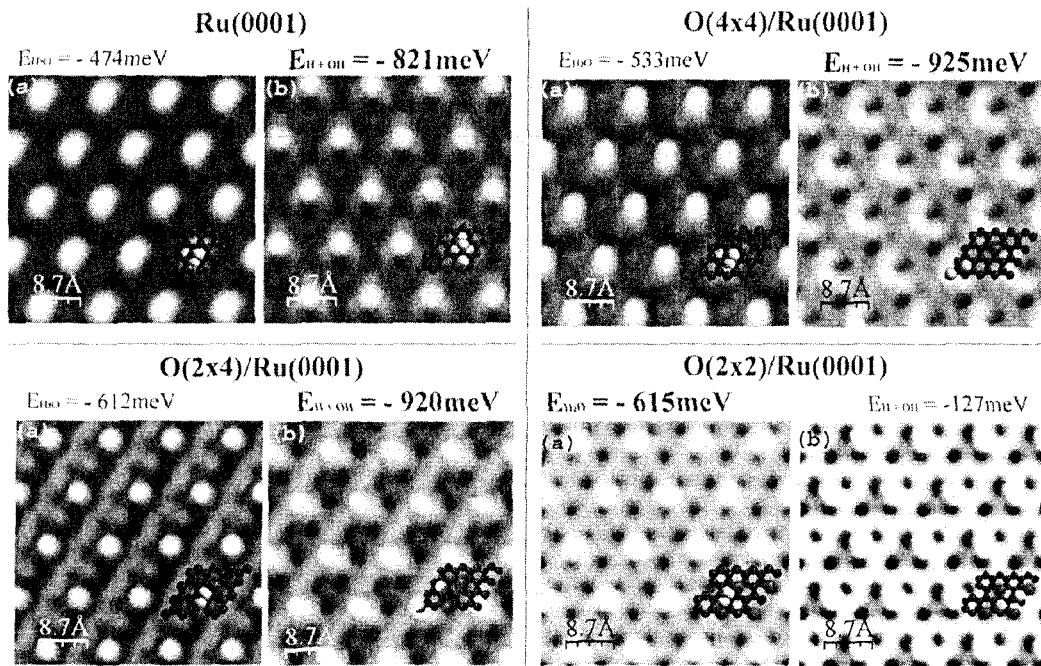E_{H_2O} = - 615meV E_{H+OH} = -127meV

Figure 1. Simulated STM images of the intact and dissociative adsorption of water on Ru(0001) surface previously exposed to different coverage of Oxygen.

(1)   Cabrera-Sanfelix, P.; Arnau, A.; Mugarza, A.; Shimizu, T. K.; Salmeron, M.; Sanchez-Portal, D. *Physical Review B* **2008**, *78*.
(2)   Cabrera-Sanfelix, P.; Arnau, A.; Sanchez-Portal, D. *Submitted* **2009**.

The quantum nature of the proton in water-hydroxyl overlayers on metal surfaces

Angelos Michaelides

London Centre for Nanotechnology and Department of Chemistry,

University College London, London WC1E 6BT, U. K.

The first layer of water on many surfaces is comprised of mixed arrangements of water and hydroxyl molecules. We show here with an ab initio approach (density-functional theory in conjunction with path-integral molecular dynamics) that such overlayers on transition metal surfaces exhibit pronounced quantum nuclear effects. The metal substrates serve to reduce the classical proton transfer barriers within the overlayers and, in analogy to ice under high pressure, to shorten the corresponding intermolecular hydrogen bonds.

Depending on the substrate and the intermolecular distance it imposes on the overlayer, the traditional distinction between covalent and hydrogen bonds within the overlayers is lost partially (e.g. on Pt(111)) or almost entirely (e.g. on Ni(111)). This, in turn, has a marked effect on the oxygen sublattice.

The key implications of this work are:

(i) quantum nuclear effects have a profound impact on the nature and structure of the hydrogen bond at interfaces and should therefore not be overlooked;

(ii) a platform on which the magnitude of quantum nuclear effects in hydrogen bonds can be systematically tuned and probed experimentally and theoretically has been identified.

Secondary structure of H-bonded Polyalanine peptides in vacuo: Computational spectroscopy and Density Functional Theory

Mariana Rossi, Volker Blum, Peter Kupser, Gert von Helden, Frauke Bierau,
Gerard Meijer and Matthias Scheffler

Hydrogen bonds are essential in stabilizing the secondary structure of polypeptides in vacuo. We here address the structure of Alanine-based peptides Ac-Ala_n-LysH+ (n=5,10,15), for which a helical secondary structure was indicated by earlier gas-phase experiments [1].

Using van der Waals corrected [2] density-functional theory (DFT) as implemented in the all-electron FHI-aims code [3], we present vibrational "computational spectroscopy" for all three molecules. Our results are corroborated by comparing calculated vibrational spectra to multiple photon IR spectroscopy data, obtained at the FELIX free electron laser for the molecules at room temperature. For the longer molecules (n=10,15), \alpha-helical structure models provide good qualitative agreement between theory and experiment already in the harmonic approximation.

For Ac-Ala_5-LysH+, an unambiguous helical structure assignment is questioned in the literature [4]. We thus perform an extensive conformational search, pre-screening O(10^5) conformers, using the opls-aa force field and different H-bond constraints in order to explore different structure families. A wide range of the resulting structure candidates (125 structures total) was post-relaxed in DFT.

The predicted lowest energy structure ("g-1") in van der Waals corrected DFT (PBE, revPBE and BLYP) is not a simple helix, showing instead an "inverted" hydrogen bond (oriented against a possible helix dipole). The qualitative differences between the harmonic spectra of different structure prototypes (g-1, \alpha- or 3_10-helical) do not yet allow for an unambiguous structure verification. Computing anharmonic spectra through Born-Oppenheimer molecular dynamics and the dipole-dipole autocorrelation function (300 K), there are marked improvements, and the predicted "g-1" conformer is clearly consistent with experiment and expected to be relevant even at finite T, where different conformers might coexist.

[1] R. Hudgins et al., J. Am. Chem. Soc 120, 12974 (1998)
[2] A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. 102, 073005 (2009)
[3] V. Blum et al. Comp. Phys. Comm. (2009), accepted
[4] M. Kohtani and M. F. Jarrold, J. Am. Chem. Soc. 126, 8454 (2004)

Study of mobile protons in enzymes as revealed by subatomic x-ray and neutron diffraction experiments

Raul E. Cachau
Science Applications International Corporation (SAIC)-Frederick
National Cancer Institute, Frederick (USA)

We will present an analysis of proton dynamics in enzymes base on combined studies of the enzyme human aldose reductase (h-AR, 36 kDa) using single-crystal x-ray data (0.66 √Ö, 100K; 0.80 √Ö, 15K; 1.75 √Ö, 293K), neutron Laue data (2.2 √Ö, 293K), and quantum mechanical modeling. These complementary techniques unveil the internal organization and mobility of the hydrogen bond network that defines the properties of the catalytic engine, explaining how this promiscuous enzyme overcomes the simultaneous requirements of efficiency and promiscuity offering a general mechanistic view for this class of enzymes.

Dynamics of Proton Transfer in Biological Systems

Janez Mavri
National Institute of Chemistry
Hajdrihova 19, SI-1001 Ljubljana, Slovenia

Proton transfer is associated with several biological processes that include enzymatic reactions, signalling process and transport. Quantization of nuclear motion is of prime importance for hydrogen bonded systems and enzyme centers. Car-Parrinello molecular dynamics (CPMD) study was performed for anharmonic systems – intramolecularly hydrogen-bonded systems, to investigate the vibrational spectrum associated with the O-H stretching in Mannich base [1,2] and picolinic acid N-oxide [3]. The proton potential snapshots were extracted from the trajectory. The vibrational Schrödinger equation for the snapshots was solved numerically and the (O-H) envelope was calculated as a superposition of the 0 to 1 transitions. The potential of mean force for the proton stretching mode was calculated from the proton wavefunctions. Perspectives will be given for application of various computational methods to address tunneling in enzymatic reactions. Calculation of large H/D kinetic isotope effect in lipoxygenase will be presented [4,5]. Relevance of nuclear quantum effects for enzymatic catalysis will be discussed.

pKa calculations of histamine and several carboxylic acids including bilirubin will be discussed in terms of their transmembrane transport [6,7].

[1] A. Jezierska, J. J. Panek, A. Koll and J. Mavri, J. Chem. Phys., 126 (2007) 205101-9.
[2] A. Jezierska, J. J. Panek, U. Borštnik, J. Mavri and D. Janežič, J. Phys. Chem B, 111 (2007) 5243-5248.
[3] J. Stare, J. Panek, J. Eckert, J. Grdadolnik, J. Mavri and D. Hadži, J. Phys. Chem A, 112 (2008) 1576-1586
[4] M.H.M. Olsson, J. Mavri and A. Warshel, Phil. Trans. Roy. Soc. B, 361 (2006) 1417-1432.
[5] J. Mavri, M.H.M. Olsson and A. Warshel, J. Phys.Chem. B, 112 (2008) 5950-5954.
[6] K. Perdan-Pirkmajer, J. Mavri and M. Kržan, to be sub.
[7] R. Borštnar, A. Roy Choudhury, J. Stare, M. Novič, J. Mavri, ChemPhys Chem, sub. 9/2009.

Title:
Proton momentum distribution of water confined in nanopores, protein hydration shells and DNA

Speaker:
Roberto Senesi
Università degli studi di Roma Tor Vergata and Centro NAST

Abstract:

Experimental determinations of proton momentum distribution on water adsorbed in silica MCM-41, in weakly hydrated proteins and DNA will be presented. The measurements have been carried out through deep inelastic neutron scattering. The results provide an insights into the short-scale dynamics and effective single-particle potential of water protons in these environments. In particular, the water-silanols interactions, the proton delocalization on the protein surfaces, and the zero-point contributions to DNA energetics will be discussed.

References:
-   S. E. Pagnotta, F. Bruni, R. Senesi, A. Pietropaolo , *Biophys. J.* **96**, 1939 (2009).
-   P.Sozzani, S. Bracco, A. Comotti, R. Simonutti, P. Valsesia, Y.Sakamoto, O. Terasaki Nature Materials 5(7), 545-551 (2006).
-   V. Garbuio, C. Andreani, S. Imberti, A. Pietropaolo, G. F. Reiter, R. Senesi, M. A. Ricci, *J. Chem. Phys.* **127**, 154501 (2007).

Title:
Hydrogen-bonding in
bi-component supramolecular nanoporous networks

Authors:
Jonas Björk*, Matthew S. Dyer and Mats Persson
Surface Science Research Centre and Department of Chemistry,
University of Liverpool, Liverpool, UK

Carlos-Andres Palma and Paolo Samori
Nanochemistry Laboratory, ISIS - CNRS 7006,
Universite de Strasbourg, Strasbourg, France

Massimo Bonnini
BASF SE, GKD/I
Ludwigshafen, Germany

Anna-Llanas Pallas and Davide Bonifazi**
Dipartimento di Scienze Farmaceutiche,
Universita` degli Studi di Trieste, Trieste, Italy
** also at
Department of Chemistry, University of Namur, Namur, Belgium

* Presenting author

Abstract:

We study the formation of four supramolecular bi-component networks based on four linear modules (linkers) bridging melamine via triple hydrogen-bonds. Scanning tunnelling microscopy (STM) experiments together with density-functional theory (DFT) calculations were used to explore the polymorphism and phase segregation, which rule the generation of highly crystalline nanoporous networks at the solid-liquid interface. The investigated linkers include two systems exposing diuracil groups in the Œ± and œâ position, naphtalene tetracarboxylic diimide and pyromellitic diimide. In situ STM investigations revealed that, when blended with melamine, the first three systems are able to form two-dimensional porous architectures. Two of the linkers, exhibit highly ordered hexagonal structures while the third one gives a polymorph structure consisting of a variety of polygons. However, the fourth linker, pyromellitic diimide, assembles only into one-dimensional supramolecular arrays. DFT calculations of the hydrogen-bond energies for the different systems were able to show that the distribution of polygons depends on the backbone flexibility of the linkers. These comparative studies offer new insights into strategies towards the bottom-up fabrication of highly ordered tunable nano patterning at interfaces mediated by hydrogen bonds.

ABSTRACTS

OF

POSTERS

(in alphabetical order of author name, as of 20 October 2009)

Adaptive force matching: a systematic way of generating high quality force fields from QM/MM calculations

Omololu AKIN-OJO

Boston University
Department of Chemistry
MA 02215, Boston, U.S.A.

and

ICTP, Condensed Matter Section
Trieste, Italy

Abstract:

Force fields are crucial for molecular dynamics simulations. Obtaining a high quality force field in condensed phase is frequently a difficult task. We present an efficient method to obtain such force fields from high level quantum mechanics/molecular mechanics (QM/MM) calculations. The method is applicable to large systems and is able to produce low cost but accurate force fields by extracting quantum information from QM/MM calculations.

NMR parameters of small water clusters

G. Bilalbegovic,
Department of Physics, Faculty of Science, University of Zagreb,
Bijenicka 32, 10000 Zagreb, Croatia

Typical small water clusters with $16^{\wedge}O$ and $17^{\wedge}O$ atoms are analyzed within a density functional theory method [1]. The gauge including projector augmented wave (GIPAW) model is used [2]. GIPAW is based on pseudopotentials and it is possible to use it for bulk, surfaces, nanotubes and clusters of a growing number of materials. In this work hydrogen and oxygen chemical shifts and $17^{\wedge}O$ quadrupole nuclear magnetic resonance parameters are calculated. Large fluctuations of chemical shifts are found for atoms in isomer clusters. Quadrupole coupling constants decrease and asymmetry parameters increase if compared with bulk water. Although the GIPAW method is not so computationally expensive as quantum chemical methods, it gives reliable results for NMR parameters in water nanoparticles.

[1] P. Giannozzi et al, J. Phys.: Condens. Matter (2009), to be published.

[2] C. J. Pickard and F. Mauri, Phys. Rev. B (2001), 63, 245101

Solvent occupancy analysis in ligand structure prediction

Santiago Di Lella, Marcelo A. Martí and Darío A. Estrin

INQUIMAE-CONICET and Departamento de Química Inorgánica, Analítica y Química Física,
Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires
Buenos Aires, Argentina

Formation of protein ligand complexes is a fundamental phenomenum in biochemistry. During the process, significant solvent reorganization is produced along the contact surface. Using MD simulations in explicit solvent combined with statistical mechanics analysis, thermodynamic properties of water molecules around proteins can be computed and analyzed in a comparative view. Based on this idea, we developed a set of analisis tools to link slvation with ligand binding in a key carbohydrate binding protein, human galectin-1 (hGal-1). Speciffically, we defined water sites (WS) in terms of the thermodynamic properties of water molecules strongly bound to protein surfaces. We then succesfully extended the analysis of the role of the surface associated water molecules in the ligand binding and recognition process to many other carbohydrate binding proteins.

Our results show that the probability of finding water molecules inside the WS, $p(v)$, with respect to the bulk density is directly correlated to the likeliness of finding an oxhydril group of the ligand in the protein-ligand complex. This information can be used to predict possible complex structures when unavailable, and suggest addition of OH- containing functional groups to displace water from high $p(v)$ WS to enhance drug, specially glycomimetic-drugs, protein affinity and/or specificity.

TEMPERATURE INDUCED PROTON MIGRATION AND PHASE TRANSITION IN DEUTERATED 3,5-PYRIDINEDICARBOXYLIC ACID

S. J. Ford (1,2), O. J. Delamore (1), J. S. O. Evans (1), M. R. Johnson (2),
G. J. McIntyre (2) and I. R. Evans (1),*

(1) Department of Chemistry, University of Durham, Durham, United Kingdom
(2) Institut Laue Langevin, Grenoble, France
*Corresponding author: ivana.radosavljevic@durham.ac.uk

Hydrogen bonds are ubiquitous in materials across the chemical spectrum, from inorganic to biological. They influence the structure, the functionality, and therefore the potential applications of materials in which they are present. [1] Of particular interest are short strong hydrogen bonds which, contrary to the primarily electrostatic nature of their weaker counterparts, possess a quasi-covalent character. Their presence can lead to interesting phenomena, such as proton migration [2] and proton order-disorder transitions. [3]

3,5-pyridinedicarboxylic acid (35PDCA) contains one of the shortest N-HÖO hydrogen bonds reported in the literature, with an NÖO separation of 2.51 ≈. [4] A two-temperature single crystal neutron diffraction study on the fully protonated compound has shown that temperature dependent proton migration occurs in this hydrogen bond. [5] At 15K, the proton is closer to the nitrogen atom, with an N-H distance of 1.213(4) ≈ and OÖH distance of 1.311(5) ≈; at 296K it has moved significantly towards the oxygen atom, resulting in an NÖH distance of 1.308(6) ≈ and an O-H distance of 1.218(6) ≈. The same effect, but more pronounced, has been found in crystals in which the carboxylic hydrogen atom positions involved in hydrogen bonding have been deuterated. In this case, the N-D distance changes from 1.151(3) ≈ at 15 K to 1.457(4) ≈ at 300 K. [5]

Variable temperature powder X-ray diffraction experiments on fully deuterated 35PDCA between 15 and 300 K, using both laboratory X-ray diffraction and high resolution neutron diffraction were carried out. [6] It was shown that in the protonated phase, the unit cell volume varied smoothly with temperature in the range observed. However, the unit cell volume variation for deuterated 35PDCA shows a change of curvature between 150 and 200 K. This effect is reversible, reproducible and it is observed both in the powder X-ray and neutron diffraction data. Also, using variable temperature single crystal neutron diffraction experiments, it was found that the deuteron position in the hydrogen bond changes gradually over the temperature range studied. This shows that, unlike in its protonated analogue, the 'proton' migration in fully deuterated 35PDCA is facilitated by a structural change.

Keywords: diffraction, migration, isotope effect

References:
[1] T. Steiner, Angew. Chem. Int. Ed., 2002, 41, 48.
[2] C. C. Wilson, Acta Crystallogr., Sect. B: Struct. Sci., 2001, 57, 435.
[3] I. R. Evans, J. A. K. Howard, J. S. O. Evans, Cryst Growth & Des., 2008, 8,165.
[4] F. H. Allen, Acta Crystallogr., Sect. B: Struct. Sci., 2002, 58, 380.
[5] J. A. Cowan, J. A. K. Howard, G. J. McIntyre, S. M. F. Lo, I. D. Williams, Acta Crystallogr.,Sect. B: Struct. Sci., 2005, 61, 724.
[6] O. J. Delamore, Durham University (Durham), 2008.

Title:
Molecular models and simulations of protic ionic liquids (PILs)

Authors:
N. C. Forero-Martinez and M. G. Del Popolo

It is well established experimentally that Protic Ionic Liquids (PILs) exhibit a first order liquid-vapour transition between a condensed phase composed mainly of ions and a gas phase formed by neutral molecules. The transition is mediated by the chemical transformation of the ions into dipolar molecules and involves a reversible proton transfer reaction between a Bronsted acid and a base. We have developed an atomistic model to investigate the condensation of the ionic liquid out of the molecular vapour in Ethylammonium Nitrate (EAN), a prototypical and well characterised PIL.

We discuss the parameterisation procedure and asses the accuracy of the model to describe the density and structure of the solid and liquid phases of EAN, as well as the ion dynamics in the liquid state.

Ferroelastic Phase Transition Solid State Chemical Reactions in $K_3H(SO_4)_2$ Crystal

V.V. Grebenev, T.S. Chernaya, I.P. Makarova, I.A. Verin, V.V. Dolbinina.
Institute of Crystallography Russian Academy of Sciences, Russia
Moscow 119333, Leninskiy pr.59, vadim.grebenev@gmail.com

It is well known that ferroelastic monoclinic (space group A2/a) phase $K_3H(SO_4)_2$ is isostructural with other crystals of the $M_3H(XO_4)_2$ family, which undergo improper ferroelastic phase transitions A2/a - $R\bar{3}m$ at elevated temperatures [1]. Evidently, a similar transition might be expected for $K_3H(SO_4)_2$. Indeed, recently a sharp increase of conductivity by several order of magnitude was found in $K_3H(SO_4)_2$ at T_{tr} = 479 K [2, 3]. However, X-ray diffraction studies performed by Chrisholm et al. [3] show that the high temperature structure of $K_3H(SO_4)_2$ (T > 479K) cannot be described as trigonal or hexagonal structure. Moreover, enthalpy and entropy of the phase transition $K_3H(SO_4)_2$ are much more than those observed for ferroelastic A2/a - $R\bar{3}m$ phase transition that observed in other crystals of $M_3H(XO_4)_2$ family [2].

The results of our recent polarised microscopy study [4] showed that phase transition in trigonal phase $K_3H(SO_4)_2$ occurs at T_{sp} = 463 K while at T > 479 K process thermal decomposition starts. However, kinetics of this ferroelastic phase transition is very slow. Therefore at usual experimental heating rates ferroelastic phase transition in $K_3H(SO_4)_2$ at T_{sp} = 463 K can be missed. Thus at thermodynamically equilibrium conditions prototype trigonal phase exists in the temperature range 463-479 K. Moreover, ferroelastic phase transition is reversible upon cooling from 479 K. On the other hand, x-ray powder diffraction data obtained above T_{sp} at equilibrium conditions indicate on the multiphase state which does not agree with single crystal state according with the optical observation data.

In this work X-ray single crystal diffraction study was carried out take into account the above mentioned peculiarities of the kinetics $K_3H(SO_4)_2$. The obtained results indicate that in temperature range 463-479 K $K_3H(SO_4)_2$ crystal belongs to $R\bar{3}m$ space group with unit cell parameters: a = 5.73(1)Å, b = 21.51(1)Å. The origin of the principal differences powder and single crystal data are discussed. Most probably that solid-state chemical reaction accompanies ferroelastic phase transition in $K_3H(SO_4)_2$ is driven by solid state chemical reactions. In part this confirmed by our X-ray powder diffraction data.

References

[1] A.I. Baranov, Crystallography Reports, 48(6), 1012 (2003). Translated from Kristallografiya, 48 (6) (2003).
[2] Chen R.H., Chang R.Y., Shern C.S., Fukami T. J. Phys. Chem. Solids 64, 553 (2003).
[3] Chisholm Calum R.I., Haile S.M. Solid State Ionics 145, 179 (2001).
[4] A.I. Baranov, V.V. Grebenev, U. Bismaer and J. Ludwig, Structural Phase Transitions and Solid State Chemical Reactions in Complex Potassium Hydrogen Sulfate Salts Driven by Fast Proton Diffusion. Ferroelectrics 369, 108 (2008).

A polarizable tight-binding model for water

Jorge Kohanoff and Tony Paxton
Queen's University Belfast
Northern Ireland, United Kingdom

Water is one of the most ubiquitous substance on Earth. It isessential for life as we know it, and it has always been the preferred solvent for chemical reactions. Therefore, the modelling of most biological and chemical processes requires a model for water. Countless models have been proposed along the past 50 years, ranging from rigid, non-polarizable units as in SPC/E to fully ab initio representations based mostly on DFT. Each class of models has found applicability within various different contexts. Classical models have been very successful in studying the properties of bulk water, and as a medium for solvation of chemical and biological species. Nevertheless, whenever water participates in the chemistry, a quantum-mechanical approach is necessary. Computer simulations using DFT-GGA approaches represented a substantial step forward in this field. However, it remains the fact that ab initio molecular dynamics simulations are computationally very demanding even with today's available resources. It is therefore desirable to devise simplified quantum-mechanical models that would allow us to study larger samples for longer times.

Here we present a self-consistent tight-binding model for water that includes charge transfer and polarization effects. It has been constructed by requiring that it reproduces the energetic, structural, electrostatic and vibrational properties of the water molecule and the water dimer as obtained from experimental data and high-level quantum-chemical calculations. Thanks to its polarizable character, the model reproduces the enhancement of the molecular dipole in clusters and in the liquid phase, and it gives a dielectric constant very close to the celebrated value of 78. Moreover, it reproduces structural and dynamical properties such as the $g(r)$ and the diffusion constant to a very good extent. We now plan to use this model to study mixed-phase catalytic systems.

Title:
Atomistic modelization of the H-bonded ferroelectric KH_2PO_4 (KDP)

Authors:
J. Lasave, (1) R.L. Migoni, (1) J. Kohanoff, (2) and S. Koval, (1)

(1) Instituto de Física Rosario – UNR (Argentina);
(2) Queen's University, Belfast (UK)

ABSTRACT

A shell model (SM) for KH_2PO_4 (KDP), the prototype compound of the family of H-bonded ferroelectric materials, has been constructed by adjusting the interaction parameters to first-principles calculations. Structural properties, energy barriers, phonons, and the relative stability between the ferroelectric (FE) phase and a relevant antiferroelectric metastable structure associated to domain walls, compare very favorably to available first-principles and experimental data. Molecular dynamics simulations show that the model behaves satisfactorily within the FE phase. This model will be used to study the elusive structure of the paraelectric (PE) phase and the nature of the FE-PE phase transition.

Nuclear quantum effects in $K_3H(SO_4)_2$-type crystals

D. Merunka and B. Rakvin

Ruđer Bošković Institute, Zagreb, Croatia

merunka@irb.hr

The H-bonded crystals of $K_3H(SO_4)_2$ (KHS) group exhibit strong nuclear quantum effects. Some of the crystals undergo an antiferroelectric phase transition in the deuterated, but not in protonated form, which is the extreme H/D isotope effect. Additionally, the absence of phase transition is usually ascribed to a quantum paraelectric state of the protonated crystal. In the quantum paraelectric state, a phase transition in a crystal is suppressed by strong quantum fluctuations of atoms, such as zero-point motion or tunneling.

To elucidate a mechanism of the quantum effects in KHS crystals, it is important to determine a proton potential in the H bond. However, the neutron scattering measurements give controversial results. The neutron diffraction measurements [1] and the low-energy peak in inelastic neutron scattering spectra [2] indicate a double-well potential and a proton-tunneling mechanism of quantum effects. However, the neutron Compton scattering measurement of proton momentum distribution [3] indicates a single-well potential and a different mechanism.

The theoretical considerations [4] show that the inconsistency between H-bond potentials derived from the position and momentum distributions of proton can be explained by the assumption that the proton does not reside in a well-defined single-particle potential, but rather in a potential that is strongly affected by a local vibrational mode of heavy atoms. The measured low-energy excitation responsible for the quantum paraelectric state is attributed to this local mode and not to the proton mode. The isotope effect is explained by different effective potentials of the local mode in protonated and deuterated crystals due to the mass effect and the geometric effect on the ground-adiabatic-state energy of proton.

[1] N. Onoda-Yamamuro, et al., J. Phys.: Condens. Matter 12, 8559 (2000).
[2] F. Fillaux, et al., Chem. Phys. 154, 135 (1991).
[3] D. Homouz, et al., Phys. Rev. Lett. 98, 115502 (2007).
[4] D. Merunka and B. Rakvin, Phys. Rev. B 79, 132108 (2009).

A Model for ferroelectric instability in H-bonded KDP-type crystals: quantum and pressure effects investigations

S. E. Mkam Tchouobiap[1,2], T. C. Kofane[1,3] and H. Mashiyama[2]

[1] Laboratory of Mechanics, Faculty of Science, University of Yaounde I, PO Box 812 Yaounde, Cameroon

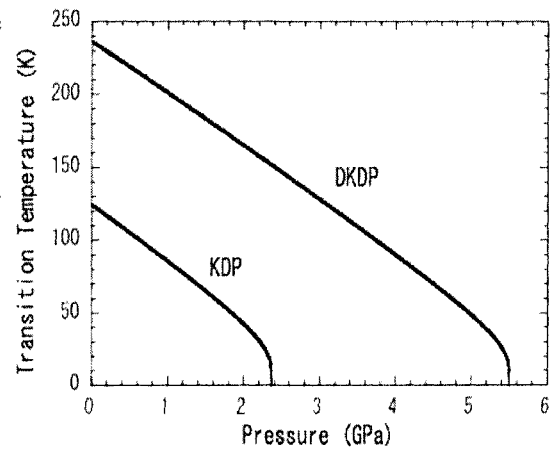[2] Department of Physics, Faculty of Science, Yamaguchi University, Yamaguchi 753-8512, Japan

[3] The Abdus Salam International Centre for Theoretical Physics, Strada Costiera 11, I-34014 Trieste, Italy

By using an extended quasiharmonic approximation to a quantum particle within an anharmonic local potential of the double-Morse type, a microscopic model for ferroelectric instability investigation in H-bonded crystals of KDP-type is proposed. The structural phase transition mechanism at low temperature is described where mean-field theory is introduced to obtain the statistical properties of the system. The quantum effect on the evolution of the ferroelectricity and phase transition is investigated. As an application, a molecular motion of H_2PO_4 in KDP is considered and the disappearance of the ordered phase at low temperature under high pressure is discussed. The difference between KDP and DKDP crystals is described successfully by the present model. Accordingly, although the ordering of protons on hydrogen bonds is the principal mechanism leading to ferroelectricity (spontaneous polarization), it is due to the local distortion of PO_4 ions. Also, it appears that motion of K is negligible.

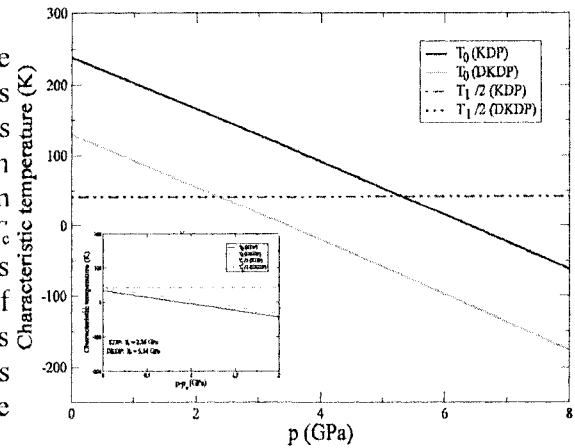Pressure dependence of the transition temperature for KDP and DKDP

Amongst other things is the large isotope effect because ferroelectric state vanishes in DKDP at a pressure over threefold than in KDP for which the obtained phase diagram seems to satisfy. Moreover, the quantum effect on transition temperature T_c is demonstrated with strong evidence if transition takes place at low temperature and, although the proton tunneling is essential in the proton (deuteron) system with double minimum potential, the decrease of T_c should be explained on the basis of quantum effects other than tunneling model. The mechanism of ordering of protons on hydrogen bonds appears as the principal mechanism leading to the spontaneous polarization in KDP-type crystals and the phase transition in KDP/DKDP is tricritical one.

Pressure dependence of characteristic temperature parameters $T_1/2$ and T_0 for KDP and DKDP. The inset shows the dependences of the two quantities $T_1/2$ and T_0 on $(p > p_c)$ in KDP and DKDP at $p > p_c$.

Also, a slight change of the model parameters of the Hamiltonian brings about a substantial change in the thermodynamic picture of the phase transition which has been confirmed experimentally and shows that the model can be applied to other KDP-type crystals.

The model builds up a picturized understanding on the physical origins of the above huge isotope effect response and its connection to geometrical effects.

Ice VII and ice VIII, and the transition between them

R.J. Nelmes, J.S Loveday, M. Guthrie, C.L. Bull, K. Komatsu, H. Hamidov, M.I. McMahon
and L.F. Lundegaard
SUPA, School of Physics and Astronomy, Centre for Science at Extreme Conditions,
University of Edinburgh EH9 3JZ

Ices VII and VIII dominate the high-pressure phase diagram of water below 70 GPa. They have been extensively studied because water is a model hydrogen-bonded system and because of the interest in the transition to proton-centred ice X which begins at ~70 GPa[1]. However, there is continuing dispute as to the precise nature of proton-disordered ice VII and its relationship to proton-ordered ice VIII. There are also reports of incommensuration in ice VII, and of discontinuities in the behaviour of both phases in the 15-20 GPa pressure range[2,3,4]. This is the region where the transition temperature (T_c) between the phases – which at low pressures is pressure independent at ~273 K – begins to fall with increasing pressure, and there are speculations that the nature of the transition changes in this pressure range[5].

We have previously completed total-scattering studies of ice VII which show that molecular orientations are disordered at nearest-neighbour distances at ~5 GPa, in keeping with measurements of the change in entropy, ΔS, for the transition from ice VIII in the same pressure range. We have now carried out comparative studies at ~20 GPa. We will also present measurements of the atomic thermal motion, which reveal anomalous behaviour in ice VIII at ~15 GPa that is associated with an apparent anomaly in the behaviour of the c/a ratio – in a range where some recent studies have shown a change in the Raman spectrum[4]. In contrast, our x-ray and neutron studies show no evidence for anomalies in ice VII around 14 GPa, contrary to the transition recently reported by Somayazulu et al[3]. Another recent study[6] found a very large change in volume per molecule, ΔV, of some 1% at ~20 GPa which implies an improbably large ΔS. We have attempted to make our own measurements and the results probably demonstrate that pressure effects make it very difficult to do this with sufficient precision. We will discuss this and the interest in measuring ΔS in this higher pressure range, and revisit what is known about the configurational entropy of ice VII and its implications for disorder models.

[1] A.F. Goncharov, V.V. Struzhkin, M.S. Somayazulu, R.J. Hemley and H.K. Mao, Science 73, 218 (1996).
[2] P. Loubeyre, R. le Toullec, E. Wolanin, M. Hanfland and D. Hausermann, Nature 397, 503 (1999).
[3] M. Somayazulu, J.F. Shu, C.S. Zha, A.F. Goncharov, O. Tschauner, H.K. Mao and R.J. Hemley, J. Chem. Phys. 128, 064510 (2008).
[4] Y. Yoshimura, S.T. Stewart, M. Somayazulu, H.K. Mao and R.J. Hemley, J. Chem. Phys. 124, 024502 (2006).
[5] P. Pruzan, J. Mol. Struc. 322, 279 (1994).
[6] H.Yamawaki, H. Fujihisa, M. Sakashita, A. Nakayama and K. Aoki, Physica B 344, 260 (2004).

HYDROGEN BONDED BIMOLECULAR MONOLAYERS ON Au(111):

A DFT STUDY

M. T. Nguyen, D. Passerone, C. Pignedoli

Empa, Swiss Federal Laboratories for Materials Testing and Research

8600 Dübendorf, Switzerland

nanotech@surfaces laboratory

Tel: +41 44 823 4074,

E-mail address: manhthuongvietnam@gmail.com

Self-assembly of molecular networks on metal surfaces plays an important role in nanotechnology. Its understanding requires the combination of accurate experiments and advanced modelling. We present a complete computational study on hydrogen bonded networks containing the popular perylene-tetracarboxylic-dianhydride (PTCDA) and diamino-p-terphenyl (DATP) on Au(111). Such networks attracted particular interest due to the possible applications in nanoelectronics. Using density functional theory with empirical van der Waals corrections, we start considering isolated adsorbed molecules and show that dispersion forces are important in determining the geometry of the interfaces, which in turn strongly affects the electronic structure. This is true both for physisorbed (PTCDA) and for weakly chemisorbed (DATP) systems. Coming to heteromolecular hydrogen-bonded self-assembled monolayers, a charge density and energy analysis shows that the surface slightly modifies the strength of hydrogen bonding between the molecules and the electronic structure. The change in work function of Au(111) due to the presence of the monolayers is mainly described in terms of Pauli repulsion and charge transfer. Our results are in excellent agreement with the experimental data, particularly concerning the scanning tunneling microscopy (STM) experiments and the relative stability of different adsorbed phases.

References:

1. M. Treier, M.-T. Nguyen, N. V. Richardson, C. Pignedoli, D. Passerone, and R. Fasel, *Nano Lett.* **9**, 126 (2009)

Hydrogen dynamics in semiconductors: a case study of crystalline and hydrogenated amorphous silicon

A.I. Shkrebtii (1,*), T. Teatro (1), L. Henderson (1), I.M. Kupchak (1,2),
Z. Ibrahim(1,3), D.V. Korbutiak (2) and F. Gaspari (1)

(1) University of Ontario Institute of Technology, Oshawa, ON, L1H 7L7, Canada
(2) V. Lashkarev Institute of Semiconductor Physics NAS, Kiev, 03028, Ukraine
(3) University of Toronto, Toronto, ON, M5S 1A7, Canada

Vibrational and optical spectroscopies are among the most sensitive and accurate tools to characterize microscopic processes in a wide class of materials. Vibrational and optical properties of amorphous hydrogenated silicon (a-Si:H) contain essential information about the microscopic dynamics of the hydrogen atoms. To decode this information from the experimental spectra, we developed a combined computational approach to comprehensively track hydrogen behaviour in both ordered (crystalline) and disordered (non-crystalline) materials, and applied it to crystalline and amorphous silicon. The a-Si:H "samples" were numerically prepared by melting, cooling down at different rates, and annealing using *ab-initio* Car-Parrinello Molecular Dynamics (CPMD). Vibrational spectra, electron density of states (DOS) and optical response were calculated at room temperature up to melting point conditions. We have identified vibrational signatures of hydrogen instability and H rebonding in the amorphous network, and formation of mono-, di- and tri-hydride Si-H complexes. Bond-center-hydrogen complexes have been observed and vibrationally characterized for both amorphous and crystalline semiconductor. Finally, a comparison with the experimental data provided a wealth of information regarding the hydrogen diffusion and quality of a-Si:H. The theoretical results are compared with experimental Fourier transform infrared spectroscopy (FTIR) and ellipsometry results. The similarities and differences between the spectra are discussed in terms of the a-Si:H properties.

The results presented are of increasing interest due to extensive application of a-Si:H in modern research and technology and to the significance of detailed microscopic understanding of the material structure, disordering mechanisms and stability. Furthermore, hydrogen by itself is an important component in amorphous semiconductors due to its passivation abilities and, recently, due to an interest in hydrogen storage using amorphous or nanomaterials systems. The novel and comprehensive parameter-free modeling technique that we developed, allows an extension to an analysis of the structural, dynamical and electronic properties of a wide class of amorphous semiconductors and non-crystalline materials.

Phase behaviour of the binary system water + oxyethylated glycerol of polymerization degree n = 25

Elena Zhyvotova, [a,*] Alexandra Zinchenko,[b] Larisa Kuleshova,[b] Eugene Dukhopelnikov,[c] Valentiva Chekanova,[b] Antonina Kompaniets,[b]

[a] National University of Pharmacy, Pushkinskaya str. 53, 61002 Kharkov, Ukraine;
[b] Institute for Problems of Cryobiology and Cryomedicine of National Academy of Sciences of Ukraine, Pereyaslavskaya str. 23, 61015 Kharkov, Ukraine;
[c] Usikov Institute of Radiophysics and Electronics of National Academy of Sciences of Ukraine, Ak. Proskura str. 12, 61085 Kharkov, Ukraine
email: elzhivotova@gmail.com

The ability of hydrogen-bonded systems to solidify in a glassy state without formation of crystals is the physical basis of action of the so-called cryoprotectants – special substances which prevent formation of ice crystals causing damage and death of biological cells below 273 K. Cryoprotectants are used for low-temperature preservation of biological objects for the purpose of transplantation or preservation of genetic material. There is a strong correlation between cryoprotecting ability and hydration ability of a compound since formation of hydrogen bonds between a cryoprotectant and water considerably decreases mobility of water molecules and prevents formation of ice crystals. Therefore study of phase behaviour and glass-forming tendency of cryoprotectant-containing aqueous solutions is of immediate practical importance.

Nowadays, oxyethylated derivatives of glycerol are considered as promising cryoprotectants [1]. In the present work, phase behaviour of the binary system water+oxyethylated glycerol of polymerization degree $n = 25$ ($OEG_{n=25}$) was studied below 273 K by DSC and optical cryomicroscopy. The hydration number characterizing intermolecular interactions was determined on the basis of DSC and IR-spectroscopy data. DSC thermograms of rapidly cooled aqueous solutions of $OEG_{n=25}$ were obtained at a low heating rate in the $OEG_{n=25}$ concentration range of 0-100 % (w/w). The phase diagram of the water+$OEG_{n=25}$ system was plotted. The diagram analysis and the cryomicroscopic data showed that crystallization of water or $OEG_{n=25}$ occurs depending on $OEG_{n=25}$ concentration. Moreover, there is a concentration range where crystallization of neither water nor $OEG_{n=25}$ occurs. According to the phase diagram analysis, one $OEG_{n=25}$ molecule can bind about 72 water molecules and about 36 of them are strongly bound. The hydration number of $OEG_{n=25}$ is found to be about 75 by IR-spectroscopy. Thus the binary system water+$OEG_{n=5}$ has sufficiently high glass-forming tendency due to containing a large number of polar groups able to form numerous hydrogen bonds with water. This fact explains high cryoprotective activity of $OEG_{n=25}$.

[1] Zhivotova, E.; Zinchenko, A.; Kuleshova, L.; Chekanova, V.; Kompaniets, A. *CryoLetters*. **2007**. *28*, 261.

TITLES

OF

POSTER

PRESENTATIONS

(in alphabetical order of author name, as of 20 October 2009)

Structure and Dynamics of Hydrogen-Bonded Systems
(26 - 27 October 2009)

co-sponsored by:
Centre for Molecular Structure and Dynamics, STFC, U.K.

TITLES OF POSTER PRESENTATIONS
(as of 20 October 2009)

Omololu AKIN-OJO (Boston University, U.S.A/ICTP, Trieste, Italy)
Adaptive force matching: a systematic way of generating high quality force fields from QM/MM calculations

Goranka BILALBEGOVIC (University of Zagreb, Croatia)
NMR parameters of small water clusters

Santiago DI LELLA (Universidad de Buenos Aires, Argentina)
Solvent occupancy analysis in ligand structure prediction

Samantha FORD (Durham University, U.K.)
Temperature induced proton migration and phase transition in deuterated 3,5-pyridinedicarboxylic acid

Nancy FORERO MARTINEZ (The Queen's University of Belfast, U.K.)
Molecular models and simulations of protic ionic liquids (PILs)

Vadim GREBENEV (RAS, Institute of Crystallography, Moscow, Russia)
Ferroelastic phase transition solid state chemical reactions in $K_3H(SO_4)_2$ crystal

Jorge KOHANOFF (The Queen's University of Belfast, U.K.)
A polarizable tight-binding model for water

Sergio KOVAL (Universidad Nacional de Rosario, Argentina)
Atomistic modelization of the H-bonded ferroelectric KH2PO4 (KDP)

Dalibor MERUNKA (Ruder Boskovic Institute, Zagreb, Croatia)
Nuclear quantum effects in K3H(SO4)2-type crystals

Serges MKAM TCHOUOBIAP (University of Yaounde I, Cameroon)
A model for ferroelectric instability in H-bonded KDP-type crystals: quantum and pressure effects investigations

Richard NELMES (University of Edinburgh, U.K.)
Ice VII and Ice VIII and the transition between them

NGUYEN Manh-Thuong (EMPA, Duebendorf, Switzerland)
Hydrogen bonded bimolecular monolayers on Au(111): A DFT study

A.I. SHKREBTII (University of Ontario, Canada)
Hydrogen dynamics in semiconductors: a case study of crystalline and hydrogenated amorphous silicon

Elena ZHYVOTOVA (National University of Pharmacy, Kharkiv, Ukraine)
Phase behaviour of the binary system water + oxyethylated glycerol of polymerization degree n = 25