



**XVIII International Conference on
"Horizons in Hydrogen Bond Research"
14-18 September 2009, Paris, France**



Book of Abstracts

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I Program

Monday 14 September

8:30-9:00 **Opening session**

Chair: Marie-Claire Bellissent-Funel

9:00-11:00 **Basic aspects of the H-Bond**

Chair: Martin Suhm

IL 1 **Paola Gilli**, University of Ferrara, Italy
p. 13 *The Nature of the Hydrogen Bond: Models and Theories*

IL 2 **Anne Zehnacker**, Laboratoire de Photophysique Moléculaire, Université Paris
Sud, France
p. 14 *Chiral recognition in the gas phase: the role of conformational isomerism and
secondary interactions*

IL 3 **Zdzislaw Latajka**, University of Wroclaw, Poland.
p. 15 *Dynamics of H-bonded systems in the gas phase, crystals and small clusters –
Car-Parrinello and Path Integral Molecular Dynamics*

IL 4 **Kersti Hermansson** , Uppsala University, Sweden
p. 16 *Is vibrational spectroscopy a good probe of H-bonding in hydroxides and
minerals?*

11:00-11:30 **Coffee break**

11:30-12:50 **Oral communications 1-4**

Chair: Poul Erik Hansen

OP 1 **Liudmil Antonov**, Bulgarian Academy of Sciences, Bulgaria
p. 50 *Smart Switches Based on Proton Transfer*

OP 2 **Oleg Filippov**, Russian Academy of Sciences, Russia
p. 51 *Unconventional bifurcate hydrogen bond*

OP 3 **Yoshiteru Matsumoto**, University of Hyogo, Japan
p. 52 *Hydrogen-bonded structures of pyrrole-solvent binary clusters studied by IR cavity
ringdown spectroscopy*

OP 4 **Majdi Hochlaf**, Université Paris-Est, France.
p. 53 *Photoionization and fragmentation of 2-pyridone monomer and dimer*

13:00-14:30 **Lunch**

14:30-16:30 **Small building blocks**

Chair: Kersti Hermansson

IL 5 **Mikhail Vener**, Mendeleev University of Chemical Technology, Moscow, Russia
p. 18 *DFT study of H-bonds in the peptide secondary structures. Side-chain-backbone
interactions and salt bridges.*

- IL 6 **Héloisa Bordallo**, Helmholtz Zentrum Berlin für Materialien und Energie,
Germany
p. 19 *The intrinsic structural behavior of the naturally occurring amino acid and its
reflection in their dynamics*
- IL 7 **Wouter Herrebout**, University of Antwerp, Belgium
p. 20 *Molecular Interactions involving Halothane, Isoflurane, Desflurane and
Sevoflurane: A Survey of Recent Experimental and Theoretical Studies*
- IL 8 **Laurence Noirez**, LLB -Saclay
p. 21 *Hidden Macroscopic Shear Elasticity in H-Bond & Viscous Liquids*
- 16:30-17:00** **Coffee break**
- 17:00-18:00** **Oral communications 5-7**
Chair: Savo Bratos
- OP 5 **Alfred Laubereau**, Physik-Department, Technische Universität München,
Germany
p. 55 *Hydrogen Bonds in Solid Hydrates of Aqueous Salts studied by Quantum
Simulations and Subpicosecond Infrared Spectroscopy*
- OP 6 **Michael Odelius**, Department of Physics, Stockholm University, Sweden
p. 56 *Probing hydrogen bonds with x-ray emission spectroscopy*
- OP 7 **Peter M. Tolstoy**, Institut für Chemie and Biochemie, Freie Universität Berlin,
Germany
p. 57 *UVNMR Study of Proton Tautomerism in Strong Anionic OHO Hydrogen Bonds*

Tuesday 15 September

8:30-11:00

Confined water

Chair:

Marie-Claire Bellissent-Funel

IL 9

p. 23

H. Eugene Stanley, Boston University, USA

Water, the "most complex" liquid: new results in bulk, nanoconfined, and biological environments

IL 10

p. 24

Toshio Yamaguchi, Fukuoka University, Japan

Thermodynamics, Structure and Dynamics of Low Temperature Confined Water

IL 11

p.25

Alenka Luzar, VCU, Department of Chemistry, USA

The role of interfacial hydrogen bonds in electric control of nanoparticle orientation

IL 12

p. 26

Sophie Le Caer, CEA, IRAMIS, SIS2M, France

Time-resolved studies of water dynamics in nanoporous media

IL 13

p. 27

José Teixeira, LLB, France

Interaction water-aminoacids. From hydration to solutions

11:00-11:30

Coffee break

11:30-13:00

Poster session

13:00-14:00

Lunch

14:00-16:30

Poster session

16:30-17:00

Coffee break

17:00-18:00

Oral communications 8-10

Chair:

Michael Odelius

OP 8

p. 59

Hiroshi Fukazawa, Neutron Materials Research Center, Japan Atomic Energy Agency, Japan

Properties of ferroelectric and hydrogen ordered ices in space

OP 9

p. 60

Giovanni Strazzulla, INAF-Osservatorio Astrofisico di Catania, Italy

H bonds in astrophysical ices

OP 10

p. 61

Oliver Kühn, Institute of Physics, University of Rostock, Germany

Two-Dimensional Infrared Spectroscopy of the Correlated Dynamics of the Adenine: Uracil Hydrogen Bonds in CDCl₃ Solution

Wednesday 16 September

8:30-10:30

Materials 1

Chair:

Werner Kuhs

IL 14

Volker Kempter, Technische Universität Clausthal, Germany

p. 29

The role of Hydrogen in interactions involving Ionic Liquids: Experimental results

IL 15

Barbara Kirchner, Lehrstuhl Theoretische Chemie, Uni Leipzig, Leipzig, Germany

p. 30

Hydrogen bonds absent and present in and at ionic liquids

IL 16

Hessel L. Castricum, Van 't Hoff for Molecular Sciences, University of Amsterdam, The Netherlands

p. 31

Hybrid organic-inorganic materials for molecular separation

IL 17

Christer B. Aakeröy, Kansas State University, Manhattan, USA.

p. 32

Constructing co-crystals using molecular sense and supramolecular sensibility

10:30-11:00

Coffee break

11:00-13:00

Oral communications 11-16

Chair:

Volker Kempter

OP 11

Virginie Marry, Université Pierre et Marie Curie - Paris 6, France

p. 62

H-Bond network in clays from molecular simulations

OP 12

Patrick Judeinstein, Université Paris-Sud 11, France

p. 63

Structure and Dynamics of Protic Ionic Liquid: NMR and neutron studies

OP 13

Valentina Venuti, Department of Physics, University of Messina, Italy

p. 64

T-dependence of the vibrational dynamics of IBP/ β -CDs inclusion complexes by FTIR-ATR spectroscopy and numerical simulation

OP 14

François-Xavier Coudert, Chimie ParisTech, France

p. 65

Water Nanodroplets Confined in Zeolite Pores: Quantifying the Strength of Hydrogen Bonds from Simulation

OP 15

Esben Ravn Andresen, Physikalisch-Chemisches Institut, Universität Zürich, Switzerland

p. 66

Nonlinear infrared pump-probe spectroscopy on a metal hydride: Insight into the ultrafast dynamics and the potential-energy surface

OP 16

Martina Roeselová, Institute of Organic Chemistry and Biochemistry ASCR, Czech Republic

p. 67

Hydrogen bonding in nanodroplets and thin water films on functionalized self-assembled monolayers

13:00-14:00 Lunch

Excursion

18:00-19:00

Meeting of the International Advisory Board Committee

Thursday 17 September

8:30-11:00 Biological systems 1

Chair: José Teixeira

IL 18 **Alberto Podjarny**, IGBMC, Department of Structural Biology, Strasbourg, France
p. 34
Mobile H-bond proton revealed by neutron and subatomic X-ray diffraction studies leads to quantum model of catalysis for Aldose Reductase

IL 19 **Joseph Parello**, University of Vanderbilt, USA
p. 35
Hydrogen bonding and hydration in calcium signaling via the EF-hand proteins

IL 20 **Patrick Senet**, Institut Carnot de Bourgogne, DIJON, France
p. 36
Dynamics, dynamical transition, and free-energy profiles along the primary sequence of proteins in native states

IL 21 **Jean-Marc Victor**, LPTMC, Jussieu, Paris
p. 37
Why proteins can slide along DNA and how they find their target

IL 22 **Peter Jordan**, Brandeis University, USA
p. 38
Normal Mode Studies of Conformational Change in Proton Sensitive Channels and Transporters

11:00-11:30 Coffee break

11:30-12:50 Oral communications 17-20

Chair: Hans-Heinrich Limbach

OP 17 **Daniela Russo**, Institut Laue Langevin, France
p. 69
Water hydrogen bond analysis on hydrophilic and hydrophobic bio-molecules sites

OP 18 **Damien Laage**, Ecole Normale Supérieure, France
p. 70
Why water reorientation slows down without iceberg formation around hydrophobic solutes

OP 19 **Paul R. Tulip**, University of Edinburgh, UK
p. 71
Peptide aggregation and solvent electrostriction in a simple model dipeptide via molecular dynamics simulation

OP 20 **David R. Nutt**, University of Reading, UK
p. 72
A dual functional role for the solvation shell of an insect antifreeze protein

13:00-14:30 Lunch

14:30-16:10 Oral communications 21-24

Chair: Patrick Senet

OP 21 **Barbara Rossi**, University of Trento, Italy
p. 73
Micro-structural investigation of SOUL protein single crystals by Raman scattering experiments and numerical simulation

OP 22 **Aurélien Perera**, Université Pierre et Marie Curie, France
p. 75
The Micro-Structure Of Liquid Water

- OP 23 **Helen Jansson**, University of Gothenburg, Sweden
p. 76 *Slow dynamics in hydrogen bonded liquids*
- OP 24 **Mehran Mostafavi**, Université Paris-Sud, France
p. 77 *Solvation Dynamics of Electron in Liquid Polyols, Solvent molecular structure effect*
- 16:10-16:40** **Coffee break**
- 16:40-17:20** **Oral communications 25-26**
Chair: Virginie Mary
- OP 25 **Huib J. Bakker**, FOM Institute AMOLF, The Netherlands
p. 78 *Water molecules in hydration shells reorient highly anisotropic*
- OP 26 **Klaas-Jan Tielrooij**, FOM Institute AMOLF, The Netherlands
p. 79 *Hydrated protons as antennas for vibrational energy*
- 17:30-19:00** **Meeting of the prize committees**
- 19:30** **Banquet**

Friday 18 September

8:30-10:00 Biological systems 2

Chair: Jean-Marc Victor

IL 23 **Erik Nibbering**, Max Born Institute, Berlin, Germany
p. 40 Hydrogen bond dynamics and proton transfer in biophysical systems

IL 24 **Alla Oleinikova**, University of Dortmund, Germany
p. 41 Percolating H-bonded networks of hydration water: specific properties and importance for biofunctions

IL 25 **Fabio Bruni**, University of Roma Tre, Italy
p. 42 Dynamic Crossovers and Quantum Effects in Protein Hydration Water

10:00-12:30 Materials 2

Chair: Martina Roeselova

IL 26 **Mary Jane Shultz**, Department of Chemistry, TUFTS University, USA
p. 44 Aqueous Hydrogen Bonding Probed with Polarization Spectroscopy on Ice

IL 27 **Werner Kuhs**, Universität Göttingen, Germany
p. 45 Water interacting with non-polar gases - lessons from gas hydrate formation and decomposition

11:00-11:30 Coffee break

Materials 2 (continued)

IL 28 **Natalie Malikova**, LLB, France
p. 46 Water and ions confined in clays - a study of transport properties

IL 29 **Lucjan Sobczyk**, University of Wroclaw, Poland
p. 47 Specificity of hydrogen bonds in protonated proton sponges and related compounds

12:30-13:00 Closing session

Chair: Marie-Claire Bellissent-Funel / Martin Suhm

II Invited lectures

II.A. Basic aspects of the H-bond

Paola Gilli, University of Ferrara, Italy

"The Nature of the Hydrogen Bond: Models and Theories"

Anne Zehnacker, Laboratoire de Photophysique Moléculaire, Université Paris Sud, France

"Chiral recognition in the gas phase: the role of conformational isomerism and secondary interactions "

Zdzislaw Latajka, University of Wroclaw, Poland.

"Dynamics of H-bonded systems in the gas phase, crystals and small clusters – Car-Parrinello and Path Integral Molecular Dynamics ”

Kersti Hermansson , Uppsala University, Sweden

"Is vibrational spectroscopy a good probe of H-bonding in hydroxides and minerals?"

IL 1: The Nature of the Hydrogen Bond: Models and Theories

P. Gilli

Department of Chemistry and Centre for Structural Diffractometry, University of Ferrara, 44100, Ferrara, Italy. E-mail: paola.gilli@unife.it

D–H...:A H-bonded interactions (D and :A = H-bond donor and acceptor) display a wide interval of binding energies, E_{HB} , from less than one to 45 kcal mol⁻¹ which, unlike normal chemical bonds, feature properties that do not simply depend on D and :A but display large variations *even for a same donor-acceptor couple*. For example, weak HO–H...OH₂ bonds in neutral water [$E_{\text{HB}} \sim 5$ kcal mol⁻¹; $d_{\text{O...O}} \sim 2.70$ – 2.75 Å] change, in acidic and basic medium, to very strong [H₂O...H...OH₂]⁺ or [HO...H...OH]⁻ bonds having $E_{\text{HB}} \sim 26$ – 31 kcal mol⁻¹ and $d_{\text{O...O}} \sim 2.38$ – 2.42 Å. These impressive differences appear to depend on two independent factors: (i) H-bonds are the stronger the more electronegative the donor (D) and acceptor (:A) atoms are, implying that any (D,A) couple defines its own *H-bond electronegativity class*, $EC(D,A)$; (ii) For a same $EC(D,A)$, H-bonds are the stronger the more similar the proton affinities of D and A are, a fact easily expressible in terms of the *PA/pK_a equalization principle* [1-3] for which really strong H-bonds can be observed only when the differences $\Delta\text{PA} = \text{PA}(\text{D}^-) - \text{PA}(:\text{A})$ or $\Delta\text{p}K_{\text{a}} = \text{p}K_{\text{a}}(\text{D}-\text{H}) - \text{p}K_{\text{a}}(\text{A}-\text{H}^+)$ tend to zero (PA being the gas-phase proton affinity and pK_a the acid-base dissociation constant in water). Molecular arrangements able to reach this condition of PA/pK_a matching have been classified as the *four strong chemical leitmotifs* [4,5].

These properties are at variance with all other types of chemical bond and can be imputed to the *dual nature of the H-bond*, which is not really ‘a bond’ but rather ‘two bonds’ formed by a same central proton with the two lone pairs located on the so-called donor and acceptor atoms. In a similar way, the H-bond energy, E_{HB} , is not the D–H...:A dissociation energy, but rather the smaller of the two bond-dissociation energies, $D_0(\text{D}-\text{H})$ and $D_0(\text{H}-\text{A})$. If one is stronger, the other is weaker so that strong H-bonds are those where $\Delta D_0 = D_0(\text{D}-\text{H}) - D_0(\text{H}-\text{A}) = 0$ and $n(\text{D}-\text{H}) = n(\text{H}-\text{A}) = 1/2$ (n = bond number).

The *dual H-bond model* leads to some important consequences:

(1) All H-bond properties are controlled by *two driving variables* to be identified in the two proton affinities, $\text{pa}(\text{D}^-)$ and $\text{pa}(:\text{A})$, or better in their linear combinations:

$$\text{H-Bond Properties} = F \{ [\Sigma\text{pa} = \text{pa}(\text{D}^-) + \text{pa}(:\text{A})]; [\Delta\text{pa} = \text{pa}(\text{D}^-) - \text{pa}(:\text{A})] \}$$

(2) In symmetric [X...H...X]⁺ and [X...H...X]⁻ bonds, $\Delta\text{pa} = 0$ by *definition* and E_{HB} reaches a maximum typical of each $EC(\text{X},\text{X})$. It can be shown that this $E_{\text{HB,MAX}}$ is proportional to $1/2D_0(\text{X}-\text{H})$ and is a linear function of $\chi(\text{X})$, the electronegativity of X.

(3) All bonds of a same $EC(\text{D},\text{A})$ have energies $E_{\text{HB}} = E_{\text{HB,MAX}} \exp[-k(d_{\text{D...A}} - d_{\text{D...A,min}})]$, where $d_{\text{D...A,min}}$ is the minimum D...A distance associated with $E_{\text{HB,MAX}}$.

(4) For a given $EC(\text{D},\text{A})$, Σpa is constant and H-bond properties depend only on the Δpa difference (*pa equalization principle*). When Δpa is expressed in terms of $\Delta\text{p}K_{\text{a}}$, H-bond energies can be appreciated by a simple tool, the *pK_a slide rule*, which collects, in form of a bar chart, the pK_a of the most common H-bond donors and acceptors (see also the poster communication “*The pK_a Slide Rule as a Tool for Predicting Hydrogen Bond Strengths*”)

Keywords: H-bond theory, PA/pK_a equalization principle, electronegativity classes

[1] P. Gilli, L. Pretto, G. Gilli, *J. Mol. Struct.* **844-845** 328-339 (2007).

[2] P. Gilli, L. Pretto, V. Bertolasi, G. Gilli, *Acc. Chem. Res.* **42** 33-44 (2009).

[3] G. Gilli, P. Gilli, *The Nature of the Hydrogen Bond. Outline of a Comprehensive Hydrogen Bond Theory*; Oxford University Press: Oxford, 2009.

[4] P. Gilli, V. Bertolasi, V. Ferretti, G. Gilli, *J. Am. Chem. Soc.* **116** 909-915 (1994).

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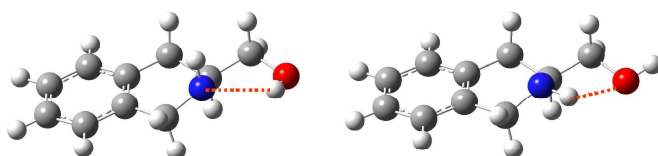
IL 2: Chiral recognition in the gas phase: the role of conformational isomerism and secondary interactions

A. Zehnacker*, A. Mahjoub, K. Le Barbu-Debus

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Chiral discrimination is of prime importance in life chemistry and is thought to occur through the formation of weakly bound complexes, involving specific interactions, like hydrogen-bonding. The study of these weakly bound diastereoisomer complexes in the gas phase brings information at the molecular level on the forces responsible for chiral recognition. Spectroscopic methods which rest on laser spectroscopy, both in the IR and UV range, are used in conjunction with quantum chemical calculations to characterise the structure of these complexes ^[1].



We will describe here structural studies of hydrogen-bonded complexes involving chiral molecules, both in neutral and ionic systems. We will show that the change in chirality of an asymmetric centre may have dramatic consequences on the nature of the hydrogen bond at play in the system, including changing its direction from OH...N to NH...O ^[2] (see figure). We will then demonstrate that the strong interactions, namely, strong hydrogen bonds, responsible for the cohesion of the complex are not in general those which are responsible for chiral recognition. Indeed, secondary interactions like OH... π or CH... π hydrogen bonds, or π stacking, play a decisive role in chiral recognition in the gas phase. Last, we will show that different isomers of a flexible molecule do not display the same efficiency in terms of chiral discrimination.

Keywords: chiral recognition, supersonic expansion, double resonance spectroscopy.

[1] A. Zehnacker, M. A. Suhm, *Angewandte Chemie-International Edition*, **47**, 6970, (2008).

[2] A. Mahjoub, A. Chakraborty, V. Lepere, K. Le Barbu Debus, N. Guchait, A. Zehnacker, *Physical Chemistry Chemical Physics*, **11**, 5160 (2009).

IL 3: Dynamics of H-bonded systems in the gas phase, crystals and small clusters – Car-Parrinello and Path Integral Molecular Dynamics

Z. Latajka

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Proton transfer in hydrogen bonds is one of the most important phenomena influencing dynamical behavior in many chemical and biological systems. In many living systems very fast proton transfer processes occur and moreover in many cases a proton behaves as a quantum particle tunneling through the energy barrier. Despite widespread importance of tunneling effects, the quantum character of proton transfer is not frequently used in theoretical models or is restricted only to the zero-temperature quantum effects in simple model systems with severe reduced dimensionality of considered systems.

The rapid development of computer power with efficient codes as well as theoretical models gives us an opportunity to study the dynamics of proton transfer processes with a great accuracy. However, the classical Molecular Dynamics with the potential derived from Molecular Mechanics (Force Fields) is not able to take into account large electron distribution accompanying the transfer of proton from one subunit to another. The Car-Parrinello Molecular Dynamics (CPMD) is very efficient scheme for description of dynamics of molecular systems. In contrary to the classical molecular dynamics the CPMD calculations do not require an a priori determined model interaction potential because the internuclear forces for each configuration of nuclei are calculated from the first principle – the model Hamiltonian is defined in the Density Functional Theory formalism. The quantum behavior of proton from a hydrogen bridge as well as remaining heavy atoms can be taken by means of the Path Integration Molecular Dynamics (PIMD).

The chemical systems with double O-H...O hydrogen bonds are very common in many chemical and biological systems. In the lecture results of CPMD and PIMD calculations will be presented for model systems with the O-H...O bonds like dimers in the gas phase, small clusters and crystals of mono- and dicarboxylic acids. The classical and quantum nature of bridged proton will be discussed.

Keywords: CPMD, PIMD, proton dynamics, carboxylic acids

IL 4: Is vibrational spectroscopy a good probe of H-bonding in hydroxides and minerals?

K. Hermansson

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One of the most established techniques for detection of hydrogen bonding is vibrational spectroscopy. A downshift of the stretching vibrational frequency of the (proposed) H-bond donor compared to its frequency as an isolated molecule is usually interpreted as a sign of H-bonding.

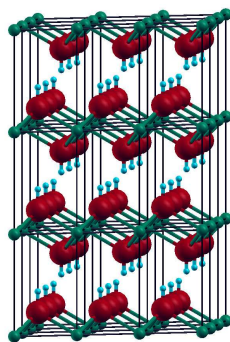
However, C–H groups sometimes exhibit upshifts (blueshifts) instead of downshifts (redshifts) when they become H-bonded. Experimental evidence for this was reported decades ago [1-3], and recently there has been an avalanche of theoretical papers on the topic.

Likewise, but less well known, is the fact that O–H groups can be both upshifted and downshifted depending on the environment. *Does a downshift always imply H-bonding? And what does an upshift imply?*

In my talk, I will discuss these questions and give examples from e.g. mineralogy, where IR and Raman spectroscopy are particularly important tools to determine local structure and bonding around H defects and OH groups.

Many minerals consist of neutral metal oxide layers with OH groups pointing towards each other across the inter-layer gap. Brucite, $\text{Mg}(\text{OH})_2$, is one example (see figure). Experiments (e.g. Ref. 4) show that the O–H stretching vibrations in brucite display a *crystal-induced OH blueshift* at ambient pressure and a *pressure-induced OH redshift* at elevated pressures. This downshift has been interpreted in the literature as an onset of hydrogen-bonding between the layers when they are pressed together. I will present an alternative interpretation of this redshift.

Some related references are found in Refs. 5-7.



Keywords: O-H vibrations, C-H vibrations, blueshift, layered minerals, ab initio calculations

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 - [2] M. Budesinsky, P. Fiedler and Z. Arnold, *Synthesis* **868** (1989).
 - [3] M.O. Bulanin, T.D. Kolomiitsova, V.A. Kondaurov and S.M. Melokova, *Opt. Spektrosk.* **68**, 763 (1990).
 - [4] M.B. Kruger, Q. Williams and R. Jeanloz, *J. Chem. Phys.* **91**, 5910 (1989).
 - [5] G. Gajewski G, P. D. Mitev and K. Hermansson, *J. Chem. Phys.* **129**, 064502 (2008)
 - [6] K. Hermansson, G. Gajewski, P.D. Mitev, *J. Phys. Chem. A* **112**, 13487-13494 (2008).
 - [7] P. D. Mitev, Grzegorz Gajewski and K. Hermansson, *American Mineralogist*, (2009). Accepted.

II.B. Small building blocks

Mikhail Vener, Mendeleev University of Chemical Technology, Moscow, Russia

"DFT study of H-bonds in the peptide secondary structures. Side-chain-backbone interactions and salt bridges."

Héloisa Bordallo, Helmholtz Zentrum Berlin für Materialien und Energie

"The intrinsic structural behavior of the naturally occurring amino acid and its reflection in their dynamics"

Wouter Herrebout, University of Antwerp, Belgium

"Molecular Interactions involving Halothane, Isoflurane, Desflurane and Sevoflurane: A Survey of Recent Experimental and Theoretical Studies"

Laurence Noirez, LLB -Saclay

"Hidden Macroscopic Shear Elasticity in H-Bond & Viscous Liquids"

IL 5: DFT study of H-bonds in the peptide secondary structures. Side-chain-backbone interactions and salt bridges

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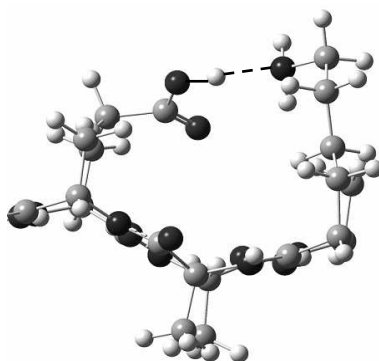
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Very recently we developed approach [1] which is based on the combined use of the DFT methods with/without periodic boundary conditions and the simultaneous consideration of the frequency shifts of the H-bonded groups and electron-density properties of the non-covalent interactions. The effects of complexity, e.g. introduction of large residues or solvent effects can be studied step by step in this treatment. It was used for the quantitative description of the H-bonds defining the intrinsic local conformational preferences of the alanine-based secondary structures. The size of the species goes up to 11 residues and all types of the secondary structures, including the protein α -helixes were studied at the same computational level. According to [1], the energies of the primary N–H...O H-bonds are decreasing in the following way: C13 > C5 \geq C7 > C10. The energies of the secondary N–H...O, N–H...N and H...H interactions are comparable to those of the primary H-bonds (\sim 4.5 kcal/mol).

This approach is applied to study the side-chain–backbone and backbone–backbone interactions in the infinite models of the alanine-based two-stranded β -sheets modified by the glycine and lysine/glycine residues, respectively. Several low-energy structures are localized by the BLYP/plane-wave computations. The minimum-energy equilibrium states of the structures are confirmed by calculating the harmonic frequencies.

The strongest side-chain–backbone interaction (\sim 11 kcal/mol) is due to the H-bond formation between the COH side-chain group and the O=C backbone group. Computed H...O=C distance equals to 1.727 Å. The frequency shift of the stretching vibration of the considered OH group, $\Delta\nu(\text{OH})$, is around 370 cm^{-1} .

The backbone–backbone interaction occurs between the glycine COH group and lysine NH₂ group, see Figure. The bridging proton locates near oxygen, however, R(O–H) = 1.021 Å. The O...N distance equals to 1.770 Å and $\Delta\nu(\text{OH}) = 771 \text{ cm}^{-1}$. The computed values indicate the formation of strong interchain H-bond. Inclusion of the solvent effects will shift the proton from O to N, i.e. it will lead to the formation of the so-called salt-bridges.



Keywords: DFT periodic boundary conditions, H-bonds, peptide secondary structures

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IL 6: The intrinsic structural behavior of the naturally occurring amino acid and its reflection in their dynamics

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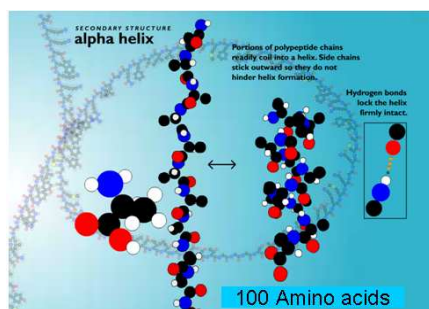
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Amino acids are biologically important materials as in their L-form, they serve as the backbones of proteins. These building blocks can be used to mimic the proteins' dominant features: their malleability in shape and internal structure, which enables them to twist and turn, with motions of different molecular fragments activated at different temperatures and time scales [1]. In this intricate ballet, subtle changes of a small molecular fragment can trigger lattice instability resulting to conformational transitions and changes in the hydrogen interactions. Crystalline amino acids show similar behavior: intramolecular conformational changes also result in lattice instabilities triggering changes of their hydrogen bond (HB) network.

Amino acids can be found in racemic form, i.e. they contain equal amounts of two enantiomers, and like so they can be used as model for racemic compounds. Racemic compounds crystallize with pairs of L- and D-molecules and surprisingly show physical properties that differ from those of the individual enantiomers. Considering that HBs – essential to biochemical processes in living systems – play a crucial role in the stability of the amino acid crystal structures, and will differentiate enantiomers and racemic amino acids, the understanding of the vibrational and structural properties of these building blocks is of general interest.

To get a better insight on the organization of the HB network of glycine polymorphs [2], L- and DL-alanine [3], L- and DL-serine [4], L and DL-cysteine [5] and L-valine we have analyzed their vibrational behavior as a function of temperature, pressure and degree of deuteration. By using Raman spectroscopy, incoherent elastic and inelastic neutron scattering we were able not only to differentiate enantiomers and racemic compounds, but also to provide further insight in particular physical properties of each building block. By combining the capability of different spectrometers a broad time range of the molecular motions could be investigated over wide temperature and pressure range. To conclude this presentation, the approach described to crystalline amino acids will be extended to small pharmaceuticals molecules.



Keywords: pressure, deuteration, Raman spectroscopy, neutron scattering

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IL 7: Molecular Interactions involving Halothane, Isoflurane, Desflurane and Sevoflurane : a Survey of Recent Experimental and Theoretical Studies

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During recent years, we have been investigating the formation of weakly bound molecular complexes with halothane, CF_3CHBrCl , isoflurane, $\text{CF}_3\text{CHClOCHF}_2$, desflurane, $\text{CF}_3\text{CHFOCHF}_2$ and/or sevoflurane, $(\text{CF}_3)_2\text{CHOCH}_2\text{F}$, by combining solutions in liquid inert gases, infrared and Raman spectroscopy, and we have determined a variety of thermodynamical and spectroscopic properties of these species. In this presentation, the experimental data obtained so far will be summarized and, where applicable, compared with theoretical results derived from ab initio calculations and/or Monte Carlo Free Energy Perturbation simulations. While describing the experimental data, special attention will be paid to specific problems caused by the presence of different conformations in isoflurane, desflurane and/or sevoflurane, the occurrence of different complexation sites in the same species, and the appearance of Fermi resonances perturbing the different C-H stretching fundamentals.

Keywords: anesthetics, cryosolutions, infrared and Raman spectroscopy

IL 8: Hidden Macroscopic Shear Elasticity in H-Bond & Viscous Liquids

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The liquid state is a condensed state of the matter that flows. Its cohesion energy is provided by intermolecular interactions, typically H-bond in glass formers, van der Waals for ordinary viscous liquids. Because of its flowing properties, the shear elastic modulus of liquids is considered to be zero. But how this cohesion energy dissipates under flow? or accommodate to flow? We show that actually liquids far away from any phase transition are not purely viscous but contain a so far neglected but non-negligible macroscopic shear elasticity; i.e. the liquid state contains solid-like correlations[1]. In the frame of the Conference, we focus on the macroscopic dynamic response displayed by a series of H-bond glass formers (glycerol, polypropyleneglycol) and also of viscous liquids (molten polymers). To extract the solid-like contribution, we examine the dynamic response of the liquid material submitted to a small (linear) mechanical oscillatory shear solicitation. Scanning the response versus frequency allows the construction of the dynamic profile in terms of elastic shear modulus (G') and viscous modulus (G''). The identification of a non-vanishing macroscopic shear elasticity ($G' \rightarrow G_0$ when the frequency vanishes) in glass formers and viscous liquids implies that long range solid-like correlations have been so far neglected. This identification of macroscopic elastic properties sheds a new light on various incomprehensible phenomena (over large time scale relaxations, spectacular flow instabilities [2,3,4]) and contradicts the conventional elementary dynamic description that gives rise to the Rouse model or reptation model for polymer chains. This description interprets the macroscopic dynamics as directly resulting from the elementary dynamic at a molecular scale (concept of "terminal time"). This single molecular picture is so far the commonly adopted description in viscoelasticity. It neglects intermolecular interactions and thus ignores the cohesive nature of the fluidic state. These new dynamic relaxation measurements restore the central role of the intermolecular interactions and of their long range elastic contribution to reinterpret the macroscopic properties of viscous liquids.

Keywords: liquid state, shear elasticity, long range correlation.

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II.C. Confined water

H. Eugene Stanley, Boston University, USA

"Water, the "most complex" liquid: new results in bulk, nanoconfined, and biological environments"

Toshio Yamaguchi, Fukuoka University, Japan

"Thermodynamics, Structure and Dynamics of Low Temperature Confined Water "

Alenka Luzar, VCU, Department of Chemistry, USA

"The role of interfacial hydrogen bonds in electric control of nanoparticle orientation "

Sophie Le Caer, CEA, IRAMIS, SCM, France

"Time-resolved studies of water dynamics in nanoporous media "

José Teixeira, LLB, France

"Interaction water-aminoacids. From hydration to solutions"

IL 9: Water, the "most complex" liquid: new results in bulk, nanoconfined, and biological environments

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This talk will introduce some of the 63 anomalies of the most complex of liquids, water. We will demonstrate some recent progress in understanding these anomalies by combining information provided by recent experiments and simulations on water in bulk, nanoconfined, and biological environments. We will interpret evidence from recent experiments designed to test the hypothesis that liquid water may display "polymorphism" in that it can exist in two different phases -- and discuss recent work on water's transport anomalies [1] as well as the unusual behavior of water in biological environments [2]. Finally, we will discuss how the general concept of liquid polymorphism [3] is proving useful in understanding anomalies in other liquids, such as silicon, silica, and carbon, as well as metallic glasses, which have in common that they are characterized by two characteristic length scales in their interactions.

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IL 10: Thermodynamics, Structure and Dynamics of Low Temperature Confined Water

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Confinement of water in a limited space occurs in nature in various fields, such as cracks in rocks, soils, cements, biological cells and many porous materials utilized for practical purposes. Well-known interesting properties of confined water are the lowering of freezing and melting temperature, crystallization of cubic ice I_c, stability of liquid state down to 140 K particularly in pores whose diameter is ~20 Å or less, etc. For understanding the unique properties and functions of confined water, it is essential to investigate the thermal behaviour, structure and dynamic properties of water confined in a nanometer space. In the present study, enthalpy and interfacial free energy changes of water were investigated in mesoporous silica MCM-41 as a function of pore size using DSC and FT-IR measurements. The results suggested that there are two stages of interfacial free energy change depending on the pore size. The microscopic structure of water adsorbed in monolayered and capillary-condensed states in MCM-41 with a pore diameter of 21 Å were examined by in-situ X-ray diffraction and neutron diffraction with isotopic substitution methods. X-ray radial distribution functions (Fig. 1) have shown that the structure of capillary condensed water in a temperature range 273~230 K is very similar to that of high-density amorphous ice in bulk, whereas that at 220~190 K is analogous to that of low-density amorphous ice in bulk. The corresponding dynamic properties of low temperature confined water were investigated by quasi-elastic neutron scattering including neutron spin echo measurements. The data on capillary-condensed water have shown a dynamical crossover in the relaxation time at 220~230 K from the Vogel-Fulcher-Tamman type (fragile liquid) behaviour above 240 K to the Arrhenius type (strong liquid) one below 220 K. Based on all the information obtained, the unique properties and function of low temperature confined water will be discussed in connection with the interfacial water in a biological system.

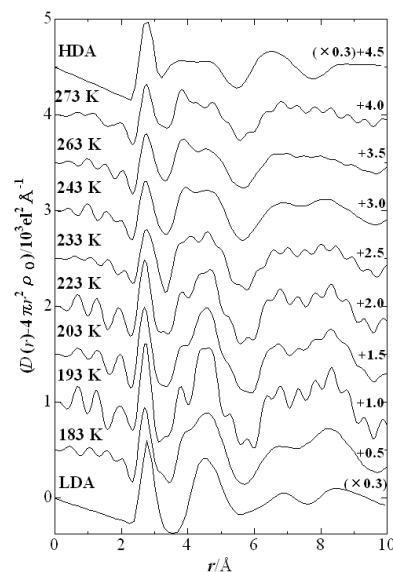


Fig. 1. X-ray radial distribution functions of capillary condensed water confined in MCM-14 C10 at various temperatures, together with those of HDA (top) and LDA (bottom) for comparison.

Keywords: confined water, interfacial free energy, liquid-liquid transition, mesoporous silica MCM-41, structure and dynamics

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IL 11: The role of interfacial hydrogen bonds in electric control of nanoparticle orientation

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Interfacial polar molecules feature a strongly anisotropic response to applied electric field, favoring dipole orientations parallel to the interface. In water, in particular, this effect combines with generic orientational preferences induced by spatial asymmetry of water hydrogen-bonding under confined geometry. The two effects are reflected in considerable dependence of water polarization on both the field direction relative to the interface, and the polarity (sign) of the field. We suggest a new mechanism to orient nanoparticles by an applied electric field even when the particles carry no charges or dipoles on their own. Coupling to the field can be accomplished through solvent-mediated interaction between the applied electric field and a nanoparticle. For nanoscale particles in water, we find the response to the applied field to be sufficiently fast that this mechanism is likely to be relevant for biological processes, for the design of novel nanostructures and sensors, and development of nanoengineering methods.

* Supported by NSF

Keywords: interfacial hydrogen bonds, electric field, nanoparticle

IL 12: Time-resolved studies of water dynamics in nanoporous media

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The behavior of water at interfaces and in confined media is poorly understood compared to its behavior in neat liquid. However, the understanding of its dynamical properties at interfaces and in confined media is of crucial importance for heterogeneous catalysis, chemistry, biology and environmental sciences.

In a first part we will present the dynamical properties of water and OH groups layered on an alumina surface studied by means of femtosecond IR-pump IR-probe transient absorption spectroscopy. The experimental results obtained demonstrate the existence of several kinds of O-H vibrators on the surface of alumina membranes, distinguishing them by their behavior on the femtosecond time scale. In the high frequency region ($> 3400 \text{ cm}^{-1}$) the absorption is due to well-packed aluminol groups and to physisorbed water patches on the surface. When pumping at 3200 cm^{-1} , physisorbed water hydrogen-bonded to AlOH_2^+ groups is observed. The excitation at 3000 cm^{-1} enables the detection of a photon-induced proton transfer reaction. From anisotropy measurements, we estimate the proton hopping time to be $900 \pm 100 \text{ fs}$ in a locally extended water network lying on the surface [1].

In a second part we will focus on confined water, i.e. HOD in D_2O confined in nanoporous silica [2]. The femtosecond IR-pump IR-probe experiments evidence that the relaxation time of confined molecules strongly depends on the probing frequency and that the molecular motions of confined water molecules are frozen. The microscopic properties of water are then modified by nanoconfinement. These results can also be linked to static IR experiments.

Keywords: nanoporous media, confined water, infrared spectroscopy

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IL 13: Interaction water-aminoacids. From hydration to solutions

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Water molecules are omnipresent in biological systems and became totally associated to life conditions. However, despite the apparent simplicity of the molecule, many fundamental problems remain open. The main problems to be understood are related to hydrogen bonds and their dynamics. In most of the biological conditions, formation of bonds between water with hydrophilic sites, establishment of specific structures around hydrophobic domains, existence of microscopic isolated water pools are only a few examples of a large variety of situations. The description of water dynamics represent a major challenge particularly because it encompasses time domains from ps to ms or more in an extreme variety of situations, often dependent on local conditions and external fields such as temperature or pH.

We performed elastic and quasi-elastic neutron scattering experiments to investigate the dynamics of side chains in proteins using, as models, hydrophobic peptides, from dry and hydrated powders up to solutions.

In concentrated solutions, when the hydrophobic side chains are hydrated by a single hydration water layer, the only allowed motions are confined, and can be attributed to librational/rotational movements associated with the methyl groups.

The parallel study of hydrated powders show a dynamical evolution from dry to highly hydrated powder and a dynamical transition at ~ 250 K for long side chain peptides while for peptides with short side chains, there is no dynamical transition but only rotational motions.

These conclusions provide a general description of the behaviour of hydrophobic entities in proteins and give information about the role of hydration water. Our results also suggest that the onset of a dynamical transition and large amplitude motions can be considered as physical characteristic of bio-molecules related with hydration water and independent of the protein function.

Keywords: Hydrogen bond, hydration, aminoacids

II.D. Materials 1

Volker Kempter, TU-Clausthal, Germany

"The role of Hydrogen in interactions involving Ionic Liquids: Experimental results"

B. Kirchner, Lehrstuhl Theoretische Chemie , Uni Leipzig, Leipzig, Germany

"Hydrogen bonds absent and present in and at ionic liquids"

Hessel L. Castricum , Institute of Petroleum Engineering, Heriot Watt University, The Netherlands

"Hybrid organic-inorganic materials for molecular separation"

Christer B. Aakeröy, Kansas State University, Manhattan, USA.

"Constructing co-crystals using molecular sense and supramolecular sensibility"

***IL 14: The Role of Hydrogen in Interactions Involving Ionic Liquids:
Experimental Results***

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The characterization and the understanding of interactions involving the C - H groups of cations of Ionic Liquids (ILs) are important for application. This holds, in particular, for ILs with cations on imidazolium (5 - membered ring, containing N and C atoms) basis.

After a short characterization of typical ILs, examples will be presented for the interaction between the cations and anions in neat imidazolium – based ILs, for the interaction of such ILs with water molecules in IL - water mixtures, and for catalyst molecules solvated in imidazolium – based ILs.

For all studied situations, it is found that C - H...X (X: O, halide atom etc. of anion; O of water etc.) interactions play an important role. It will be discussed whether these C - H...X interactions can be considered as conventional H - bonds.

IL 15: Hydrogen bonds absent and present in and at ionic liquids

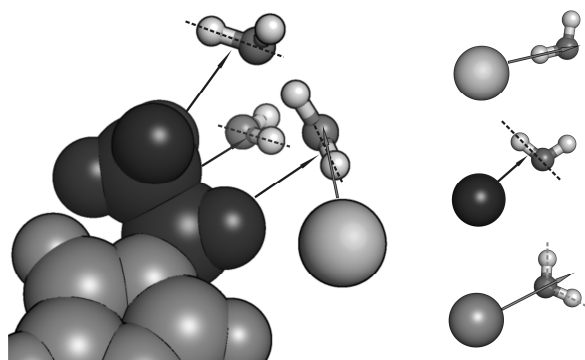
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The importance of hydrogen or intermediate bonding in ionic liquids (ILs) has been recognized by many authors. As far back as 1990, Seddon et al. showed that cation-anion contacts via hydrogen atoms of the imidazolium cation exist.[1] However, the term hydrogen bonding has to be treated with care, because depending on the kind of IL different intermediate interactions between cations and anions occur. Tsuzuki et al. showed for one example that the nature of the intermediate bond can lack directionality and therefore they concluded that a traditional hydrogen bond is not essential for the attraction.[2]

In this contribution, we present static quantum chemical calculations of different ion pairs showing that a broad variety of interactions in ILs are possible and that a classification is almost impossible.[3] We will also highlight the dynamics of the "hydrogen bond" in ILs by considering the autocorrelation function of an intermediate bond descriptor in ab initio molecular dynamics (MD) simulations.[4] Traditional MD simulations are applied in order to understand why the hydrogen bond elimination in imidazolium-based ILs leads to an increase in viscosity.[5]



In an ab initio MD simulations of a single ion pair ([Emim][Cl]) dissolved in some water molecules we find a significant increase of the IL dipole moment. Surprisingly, next to the hydrophobic groups the dipole moment of the water molecules is smaller than in the bulk indicating depolarization. The peculiar ion pair formation of [Emim][Cl] as opposed to [Na][Cl] can be understood as solvent-enhanced ion pair, i.e. water acts as a glue. [6]

Keywords: ionic liquids, intermolecular interactions, ab initio and traditional MD

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IL 16: Hybrid organic-inorganic materials for molecular separation

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We have developed a series of organic-inorganic hybrid materials with exceptional hydrothermal stability. The materials consist of an amorphous silica matrix with covalently attached organic groups. Part of the Si-O-Si has been replaced by either Si-C_xH_y-Si bridging groups or by Si-C_xH_y side groups. When applied as microporous or mesoporous thin films on a support, the materials provide excellent opportunities for long-term application as molecular separation membranes. Application of such membranes can lead to substantial energy savings as compared to currently applied highly inefficient industrial technologies such as distillation. Actual application is however critically dependent on operational stability. While a large number of relevant separations involve the presence of water, most ceramic materials are insufficiently resistant to structural changes that are induced by chemical reactions with water. We have shown that the condition of hydrothermal, and consequently operational, stability can now for the first time be satisfied with the current hybrid materials [1].

Various procedures were applied to synthesize the organosilica materials, varying from one-pot sol-gel preparation to post-modification of an existing porous silica matrix by means of grafting techniques. We found that the first method is the most suitable for the preparation of microporous (pore diameter <2 nm) materials. For homogeneous modification of the pore surface of mesoporous (p.d. >2 nm) materials, chlorotrimethylsilane was found to be the agent of choice. This procedure leads to only minor changes in the pore structure.

A fundamental study of the interaction between water and the pore surface of hydrophilic (pure silica) and hydrophobic (methyl-modified) materials has been carried out. We have studied the pore structure by nitrogen gas adsorption and NMR cryoporometry. The melting/freezing behaviour of water and ice in the pores was studied by DSC and neutron diffraction for cooling and heating cycles covering a range of 200 to 300K. Measurements were made for several filling factors in the range $f=0.2$ to 0.9. The results show a systematic difference in the form of ice created in each of the samples. The non-modified sample gives similar results to previous studies with hydrophilic silicas, exhibiting a defective form of cubic ice superimposed on a more disordered pattern that changes with temperature and has been characterized as 'plastic' ice. The modified sample has similar general features but displays important variability in the ice transformation features, particularly for the case of the low filling-factor ($f=0.2$). The results are of relevance for further tailoring of hybrid materials towards specific molecular separation applications.

Keywords: hydrophilic/hydrophobic materials, pore characterization, molecular separation

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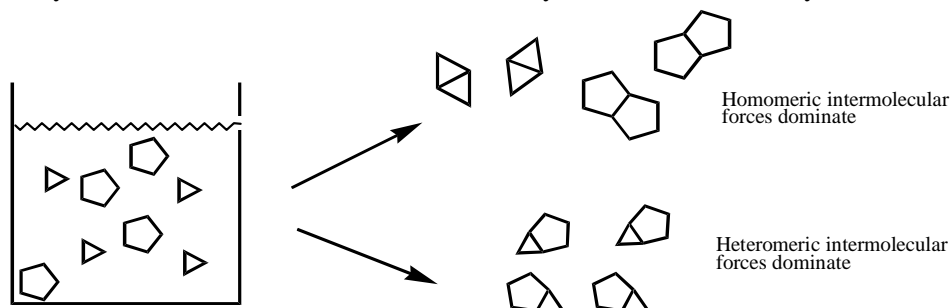
IL 17: Constructing co-crystals using molecular sense and supramolecular sensibility

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What is the most likely outcome when a homogeneous solution containing two different molecular solutes is allowed to evaporate to dryness? Unless a chemical reaction driven by the formation of covalent bonds takes place between the two solutes, one would, as a rule, expect the appearance of two separate molecular solids – the equivalent of a simple recrystallization. In the supramolecular laboratory, however, the very same process provides an opportunity to move in a completely different direction – a co-crystallization is a deliberate attempt at bringing together different molecular species within one periodic crystalline lattice without making or breaking covalent bonds. Recrystallization and co-crystallization processes are, in essence, only distinguishable by their intents. The goal of the former is a homomeric product, whereas the latter procedure strives for a heteromeric product and, in general, the odds are stacked firmly in favor of a homomeric product, Scheme 1, so how do we go about developing reliable, effective, and versatile synthetic methods for the directed assembly of heteromeric co-crystals?



This presentation will (a) outline practical strategies for modular and directed assembly of co-crystals and (b) demonstrate how different physical properties of an active ingredient (such as a pharmaceutically relevant compound) can be altered through co-crystal synthesis.

Keywords: co-crystals, molecular recognition, crystal engineering

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II.E. Biological systems 1

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"Mobile H-bond proton revealed by neutron and subatomic X-ray diffraction studies leads to quantum model of catalysis for Aldose Reductase"

Joseph Parello , University of Vanderbilt, USA

"Hydrogen bonding and hydration in calcium signaling via the EF-hand proteins"

Patrick Senet , Institut Carnot de Bourgogne, DIJON, France

"Dynamics, dynamical transition, and free-energy profiles along the primary sequence of proteins in native states"

Jean-Marc Victor, LPTMC, Jussieu, Paris

"Why proteins can slide along DNA and how they find their target"

Peter Jordan, Brandies University, USA

"Normal Mode Studies of Conformational Change in Proton Sensitive Channels and Transporters"

IL 18: Mobile H-bond proton revealed by neutron and subatomic X-ray diffraction studies leads to quantum model of catalysis for Aldose Reductase.

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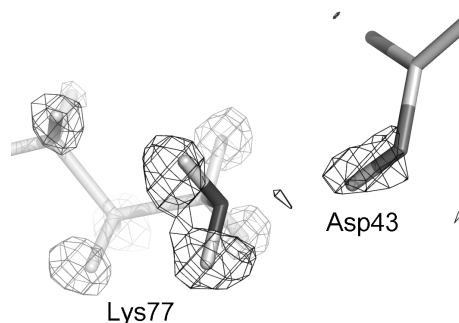
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The enzymatic mechanism of Human Aldose Reductase (*h*-AR) includes a hydride donation from the coenzyme NADPH and a proton donation from the enzyme. X-ray electron density maps solved at very high resolution of *h*-AR complexes with different inhibitors (IDD-594, 0.66 Å; IDD-552; IDD-393; Fidarestat, 0.90 Å) show within the active site crucial protonation states. However, the details of the proton donation mechanism remained unclear.

To address this question, fully deuterated protein (*h*-AR(D), ILL, Grenoble) was studied both by X-Ray and neutron diffraction methods at room temperature[1]. The identity between the complexes of *h*-AR(D) and of *h*-AR(H) was demonstrated by a helium-cooled X-Ray structure of *h*-AR(D) (resolution 0.8 Å, CA rms difference(H-D)=0.1 Å; 15K, collected at SBC 19ID APS synchrotron). Neutron Laue diffraction data from *h*-AR(D) complexed with the inhibitor IDD594 and NADP⁺, were collected to a resolution of 2.2 Å at room temperature at LADI-I. X-Ray room temperature data were also collected to 1.8 Å at the Swiss Light Source synchrotron. Both data sets were used in a joint refinement, in which the neutron data played a key role.

The catalytic site includes the residues Asp43-Lys77-Tyr48, which are connected by H-bonds. The analysis of both the X-ray maps from the *h*-AR(D) structure at 0.8 Å (see figure) and the neutron maps suggested the mobility of the hydrogen atom in the H-bond Asp43-Lys77, and therefore the presence of a neutral form of Lys77. This observation allowed the validation a MD-QM model of the proton donation. In this mechanism the neutral form of Lys77 approaches the catalytic residue Tyr48, which donates the proton to the substrate. The energy pathway will be described, showing that hydride donation is followed by barrier-free proton donation.

The combined use of experimental determination of hydrogen positions and quantum modelling has thus shown how the mobility of an H-atom inside an H-bond is crucial for an enzymatic reaction.



Keywords: enzyme catalysis ; neutron diffraction ; quantum mechanics

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IL 19: Hydrogen bonding and hydration in calcium signaling via the EF-hand proteins

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Calcium signaling in cells involves a large family of calcium-binding proteins (CBPs) termed the EF hand CBPs. The EF hand domain is composed of a structurally conserved helix-loop-helix (HLH) motif with both alpha helices (with ten residues each) flanking the central calcium-binding loop (with ten residues). The HLH motif mostly appears as pairs forming a well-defined functional assembly with two structurally correlated calcium binding sites. The EF hand-CBPs differ by the number of such assemblies. Most of the EF hand-CBPs have been demonstrated to bind magnesium ions so that these proteins alternate between their calcium- and magnesium-loaded forms depending on the ion content and distribution within the cell during time. In the case of the EF hand parvalbumin with two HLH domains, our laboratory has shown that: (i) calcium is heptacoordinated in a pentagonal bipyramidal configuration; (ii) magnesium is hexacoordinated in a regular octahedral configuration. As part of an evolutionary study of parvalbumin it was shown that specific water-binding sites are totally conserved during evolution. One water molecule directly coordinates the central cation in one of the HLH domains. Its significance in the functioning of the EF hand-CBPs will be discussed. The discovery of a conserved water site in parvalbumin that is involved in specific hydration of a kinked alpha helix has led to the search of such specific water-protein interactions in the CBPs. The possible role of a hydrated kinked alpha helix in CBP functioning as well as in the functioning of proteins in general will be discussed.

IL 20: Dynamics, dynamical transition, and free-energy profiles along the primary sequence of proteins in native states

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A protein in its 'native state' is an ensemble of structures stabilized by the competition between intra-molecular interactions and protein-solvent interactions. The free-energy landscape (FEL) resulting from these interactions is "rugged" with multiple minima. Consequently, the dynamics of a protein is complex, with multiple relaxation times. Understanding how a single native protein diffuses on its FEL and how the FEL depends on the properties of water, is essential to understand protein kinetics and function. The multi-dimensional FEL of a protein is hard to visualize but it can be projected along internal coordinates of its backbone [1] and of its side-chains [2]. Using all-atom molecular dynamics simulations (MD), a primary sequence of one-dimensional free-energy profiles (FEP) of a protein can be constructed theoretically [1, 2]. The dynamics along these FEP and along the primary sequence can be related to the temporal fluctuations of local probes and to fluorescence anisotropy and NMR [2].

In the present work, the FEP along the primary sequence of different proteins [seven 46-residues α/β thionins, a 20-residues β -sheet, and a 641-residues Heat Shock Protein (HSP)] have been computed and analyzed by using all-atom MD [1-4]. The results are presented in three parts. **Native state at 300 K** [1,2]. The diffusion of the backbone and of the side-chains along their respective FEP in the native state is anomalous (on 10 ns time-scale) and is characterized by auto-correlation functions which are power-laws of time, t^α , with an exponent α smaller than 1. The exponent is related to the existence of activation barriers along the FEP which can be detected by measuring dynamical correlation functions on short (100 ps) time-scale. **Dynamical transition at 200 K** [3]. The dynamical transition and its dependence on the primary sequence is studied within a protein family (thionins). We show how the activation of water diffusion around 200 K modifies the free-energy profiles and the dynamics of main chains of proteins. **Conformational dynamics of a multi-domain protein** [4]. Preliminary results of the analysis of the FEP of HSP and their relation with intra-molecular interactions, conformational changes, and ligand binding are briefly discussed.

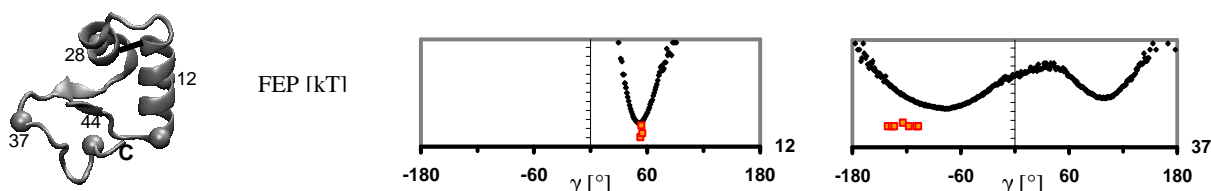


Figure. Left: typical structure of a thionin (numbers indicate the positions of residues in the sequence). Middle: FEP of residue 12 in crambin at 300 K. Right: FEP of residue 37 in crambin at 300 K. FEP are along an internal coordinate of the backbone (dihedral angle γ , see [1]) and have been computed by using MD. Squares are the values of γ deduced from NMR-derived structures. See details in [1].

Keywords: free-energy, water, dynamical transition, conformational dynamics

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IL 21: Why proteins can slide along DNA and how they find their target

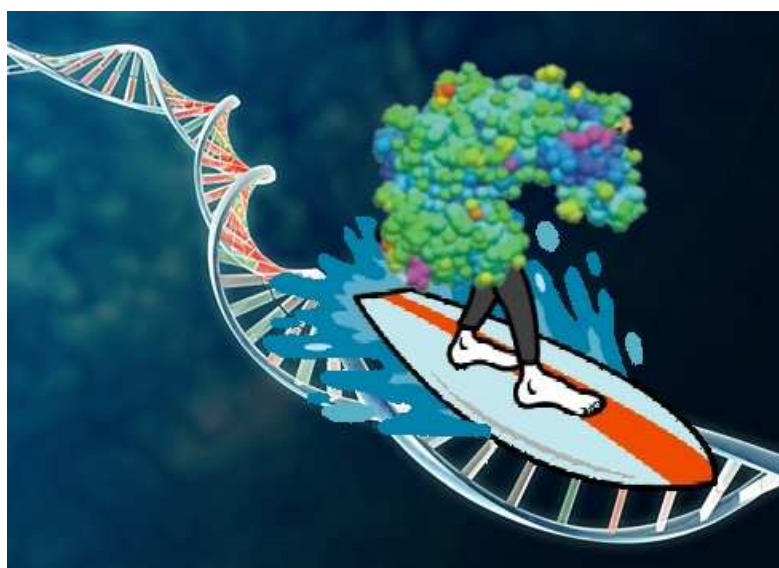
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Recent single molecule experiments have reported that DNA binding proteins (DNA-BPs) can diffuse along DNA [1]. This suggests that interactions between proteins and DNA play a role during the target search even far from their specific site on DNA. Here we show by means of Monte Carlo simulations and analytical calculations that there is a counterintuitive repulsion between the two oppositely charged macromolecules at a nanometer range. For the concave shape of DNA-BPs, and for realistic protein charge densities, we find that the DNA-protein interaction free energy has a minimum at a finite surface-to-surface separation, in which proteins can easily slide. When a protein encounters its target, the free energy barrier is completely counterbalanced by the H-bond interaction, thus enabling the sequence recognition [2].



Keywords: DNA-Binding protein, Poisson-Boltzmann equation, Monte Carlo simulation

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IL 22: Normal Mode Studies of Conformational Change in Proton Sensitive Channels and Transporters

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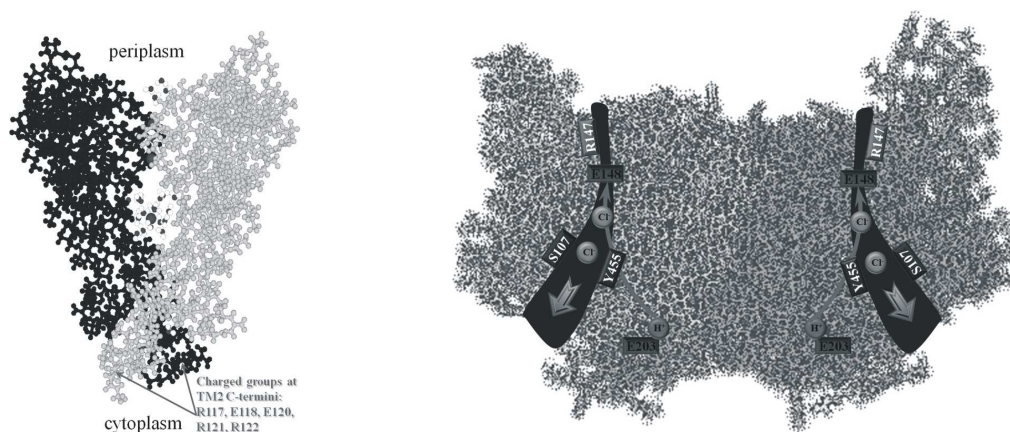
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Normal Mode Analysis (NMA) is a powerful tool for identifying and illuminating the cooperative, lowest frequency, longest wave length, motions governing conformational change in macromolecules [1]. Using traditional and enhanced methods, we study gating in two proton sensitive prokaryotic systems: the potassium selective ion channel, KcsA, and the chloride selective antiporter, CIC-ec1. The insights gleaned are directly relevant to eukaryotic systems.

Potassium channels fluctuate between closed and open states. We showed that *proton catalyzed* gating in KcsA involves rotation and unwinding of the TM2 bundle, lateral movement of the TM2 helices away from the channel axis, and disappearance of the TM2 bundle [2]. Later experiment [3] clearly revealed that upon opening the intracellular pore, rotational motions around the protein's longitudinal axis predominate and far exceed the helices' radial expansion. Opening the intracellular gate required cytoplasmic acidification of a network of ionizable residues, breaking salt bridges, requiring protonating both cytoplasmic residues, E118 and E120 [2]. Subsequent experiment [4] showed that protonating these glutamates is essential for gating.

CIC chloride channels and transporters have wide-ranging physiological roles. One family member, CIC-ec1, was structurally resolved and subjected to extensive functional modification. It is a Cl⁻/H⁺ antiporter, not a Cl⁻ channel; the molecular mechanism for Cl⁻/H⁺ exchange remains a mystery. We explore possible antiport mechanisms and propose that the exchange involves a conformational cycle of alternating exposure of Cl⁻ and H⁺ binding sites of both CIC pores to the two sides of the membrane, during which the proton sensing residues E203 are alternately accessible and inaccessible to the intracellular solution.



Keywords: potassium channels, chloride transporters

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II.F. Biological systems 2

Erik Nibbering , Max Born Institute, Berlin, Germany

"Hydrogen bond dynamics and proton transfer in biophysical systems"

Alla Oleinikova , University of Dortmund, Germany

"Percolating H-bonded networks of hydration water: specific properties and importance for biofunction"

Fabio Bruni, University of Roma Tre, Italy

"Dynamic Crossovers and Quantum Effects in Protein Hydration Water"

IL 23: Hydrogen bond dynamics and proton transfer in biophysical systems

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Using ultrafast two-colour infrared pump-probe and multidimensional photon echo spectroscopies key insight can be obtained into the dynamics of hydrogen bonded molecular systems, ranging from well-defined molecular motifs, such as acetic acid dimer, to disordered highly fluctuating liquids, e.g. water [1]. Here excitation of intramolecular OH stretching and OH bending vibrations, but also of hydrogen bond vibrations (such as librational modes) can be used as marker modes to probe a large variety of dynamical processes of the hydrogen bonded networks. For example, measurement of spectral diffusion enables the determination of the time scale for hydrogen bond rearrangements (including translational and angular fluctuations, and breaking and formation of hydrogen bonds) [2], generation of coherent wave packet motions provides information on anharmonic couplings between high frequency OH stretching and low-frequency hydrogen bond modes, and with detection of vibrational population dynamics the energy flow pathways can be derived.

Following infrared-active marker modes it is possible to determine the sequential proton transfer dynamics of an optically triggered photoacid to accepting carboxylate bases in aqueous solution [3]. Characteristic time scales can be derived for the peripatetic pathways for proton exchange between acids and bases, that follow a correlation between the reaction rates and the free energy of the reaction, from which it becomes clear that the solvent water plays a key role in the dynamics.

In this talk I will highlight some recent advances in the ultrafast hydrogen bond dynamics of hydrated DNA and ultrafast photoinduced proton transfer in aqueous solution. We have measured the vibrational dynamics of hydrogen bonded adenine-thymine base pairs in 23-oligomer double helix DNA in Watson-Crick geometry under controlled hydration conditions. We derive the time scales for vibrational excitation exchange between NH stretching modes and the subsequent relaxation dynamics. In addition we determine the dynamics of water in the hydration shell of DNA, where in particular the couplings between the ionic phosphate groups and bound water suggest that hydration shell water acts as a heat sink for DNA.

We have extended our ultrafast protonation studies to exploring the acid-base chemistry of cyanate anion, OCN^- , and of bicarbonate, HCO_3^- , in aqueous solution. Following the transient response in the spectral range of the cyano stretching vibrational marker modes of HOCN and HNCO reveals how much of both reaction products are formed at early delay times upon protonation of OCN^- , and whether the on-contact reactive complex between the photoacid and OCN^- has a well-defined structure. We present femtosecond infrared spectroscopic results showing unequivocal support for the existence of carbonic acid under aqueous conditions, formed after ultrafast protonation of HCO_3^- .

Keywords: dephasing and spectral diffusion, vibrational energy transfer, acid-base chemistry

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IL 24: Percolating H-bonded networks of hydration water: specific properties and importance for biofunctions

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The central role of hydration water in biofunctions is well recognized. However, it is not known, what particular properties and what particular state(s) of hydration water make the biofunctions possible. To answer this question, it is necessary to establish a clear relation between the state of hydration water and the manifestations of biological activity at various levels. Experimental studies evidence, that the conformational stability and functions of a biomolecule are possible only when the hydrogen-bonded water network spans its surface. Upon hydration of proteins, such network appears via a 2D percolation transition at a certain hydration level where the onset of biological functions occurs [1]. To clarify what particular properties of this spanning network of hydration water are crucial for biofunction, various physical properties of hydration water and of biomolecules in the states with and without this network should be compared. We have developed the methods allowing the study of the formation of a spanning network of hydration water various systems by simulations [2-7]. In model protein powder, infinite water network appears via 2D percolation transition [6] in good agreement with experiment [1]. Full dynamics of a single protein molecule is restored, when it is covered by a spanning water network, which appears via 2D percolation transition [6,7]. DNA molecule shows polymorphic transitions at the hydration level, which is strikingly close to the percolation threshold of hydration water [8]. The dynamic transition in crystalline Snase upon pressurization is caused by formation of the spanning water network enveloping each biomolecule [9]. Dynamics of hydration water [10] and counterions [11] change qualitatively at the percolation threshold of hydration water.

For the fully hydrated biomolecules, the spanning network of hydration water breaks upon heating via percolation transition at some temperature, which is close to the temperature of the unfolding transition [12] and to the narrow temperature interval, where the biological activity of the living organisms is maximal [13]. The entropy of hydration water related to the diversity of cluster size diverges at the percolation threshold that may enable the ordering processes in another part of the biosystem (biomolecules).

Keywords: hydration water, percolation, biomolecules

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IL 25: Dynamic Crossovers and Quantum Effects in Protein Hydration Water

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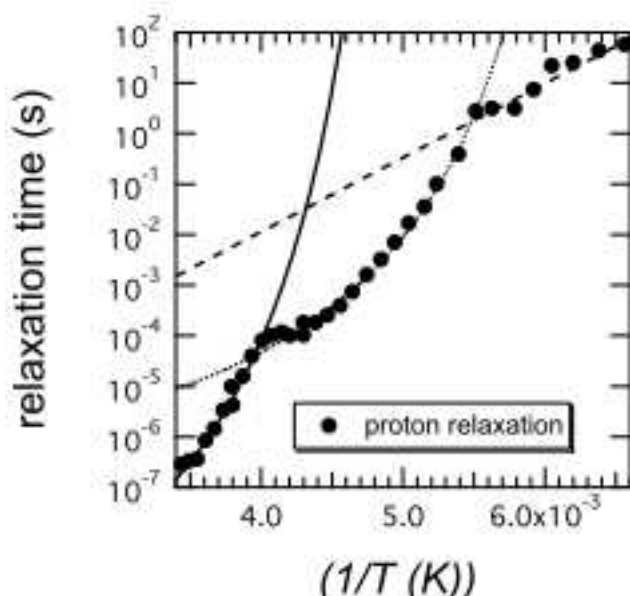
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Recent work has focused on dielectric relaxation experiments on hydrated proteins, aimed at the study of water and protein dynamics [1- 4]. At variance with these experiments, we will report on the dielectric relaxation of water protons. In particular, we discuss the temperature dependence of proton dynamics along chains of hydrogen bonded water molecules at the interface with a globular protein. The rationale behind this approach is that measurements of the proton mobility are closely linked to the dynamics and connectivity of the water molecules in the protein hydration shell.

Quantum effects on the water proton dynamics over the surface of a hydrated protein are measured by means of broadband dielectric spectroscopy and deep inelastic neutron scattering [5]



Keywords: protein hydration water, dielectric relaxation, dynamic crossovers

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II.G. Materials 2

Mary Jane Shultz , Department of Chemistry, TUFTS University, USA
"Aqueous Hydrogen Bonding Probed with Polarization Spectroscopy on Ice"

Werner Kuhs, Universität Göttingen Germany
"Water interacting with non-polar gases - lessons from gas hydrate formation and decomposition"

Natalie Malikova , LLB, France
"Water and ions confined in clays - a study of transport properties"

Lucjan Sobczyk, University of Wroclaw, Poland
"Specificity of hydrogen bonds in protonated proton sponges and related compounds"

IL 26: Aqueous Hydrogen Bonding Probed with Polarization Spectroscopy on Ice

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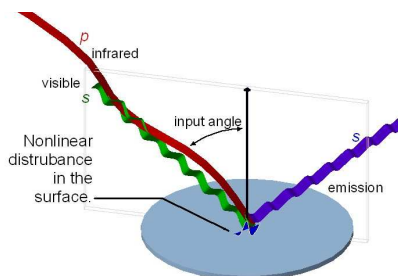
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A major challenge in hydrogen-bond research is interpreting the vibrational spectrum of water, arguably the most fundamental of the hydrogen bonding systems. This challenge remains despite over half century of progress in vibrational spectroscopy, largely due to a combination of the huge oscillator strength and the enormous width, nearly 800 cm^{-1} , of the hydrogen bonded region. Lack of assignment of the resonances in the hydrogen-bonded region hinders investigation of interactions between water and solutes. This lack-of-interpretation issue is an even more significant problem for studies of the aqueous interface. Numerous solutes are known to have an effect, some very dramatic, on the shape of the surface spectrum. These changes, however, are but tantalizing teasers because they currently cannot be used to probe the effect of solutes or impinging gas-phase molecules on the surface.

Surface vibrational spectroscopy has progressed significantly in the last two decades thanks in large part to development of equipment capable of producing sum frequency generation (SFG). SFG is a nonlinear spectroscopy that results from combining a visible and tunable infrared beam; due to symmetry, this combination occurs only at the surface. SFG thus produces a vibrational spectrum of the surface.

In the reported work, SFG is used to probe the surface of single crystal, I_h , ice. The ice surface vibrational spectrum is simpler than that of liquid water due both to the more limited thermal motion on the surface and to the periodic array of water molecules. In addition to single crystal ice, the reported work exploits the polarization characteristics of SFG to produce a polarization map for the surface vibrations, resulting in a deconvolution of the broad spectrum into at least nine underlying resonances. The polarization map aids in assigning the resonances.



In addition to the polarization map, the reported work probes both the basal and the prism faces of ice. Polarization plus multiple faces enables assignment of two resonances in the hydrogen-bonded region. One resonance is correlated with the crystal temperature and is a sensitive probe for interactions that disrupt long range order on the surface. The second is associated with weakly bonded, double-donor water molecules. This resonance is sensitive to interaction of hydrogen bond donors, i.e. acids, with the surface. Both modes are more correctly pictured as collective modes. These two assignments are the first definitive assignments for the aqueous surface.

This presentation will discuss the polarization spectroscopy as well as the specific results for ice.

Keywords: Ice, water, surface, vibrational modes, polarization

IL 27: Water interacting with non-polar gases - lessons from gas hydrate formation and decomposition

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The interaction of hydrophobic gases with water can be studied in gas clathrate hydrates in an exemplary way. It is interesting to note that in these hydrates the solubility of gases is orders of magnitude larger than in liquid water. Bridging this "solubility gap" when going from the liquid to the solid state is a particular challenge with respect to the formation of gas hydrates. Notwithstanding recent efforts by molecular dynamics simulations and X-ray reflectometry the transformation of water/ice into gas hydrates is not understood on a molecular level, despite its importance e.g. for flow assurance in gas pipelines [1]. Nevertheless, some interesting insight into these formation processes can be gained from time-resolved neutron scattering experiments [2,3]. Equally interesting are the reverse decomposition reactions accompanied sometimes by anomalous preservation phenomena [4]. Particularly intriguing are scanning-electron-microscopic (SEM) observations of gas hydrate surfaces, from which clear evidence for a mesoscopic separation of gas phase and solid ice is obtained which by all evidence takes place inside the stability field of gas hydrates [5]. This finding is further supported by synchrotron tomography showing a thickness of a few μm for this decomposed layer covering the free surface as well as grain boundaries [6]. Considering the highly dynamic nature of solid ice surfaces we suggest that these rearrangements are related to mesoscopic hydrophobic interactions in the exposed and perturbed gas hydrate surface leading to a separation of H-bonded ice (as evidenced by diffraction) and a gas phase. There is some evidence that this mesoscopic phase separation process is taking place upon rapid cooling. The resulting sponge-like ice structure with pore sizes in the order of 100 nm is well-documented by our SEM work and varies somewhat with the hydrophobic nature of the gas. Similar phenomena were suggested for the liquid state from computer simulations [e.g. 7] or observed experimentally [e.g. 8, 9] and have foundations in theoretical work on hydrophobic assembly and dewetting phenomena [e.g. 10, 11].

Keywords: gas hydrate, interface, hydrophobic assembly

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IL 28: Water and ions confined in clays - a study of transport properties

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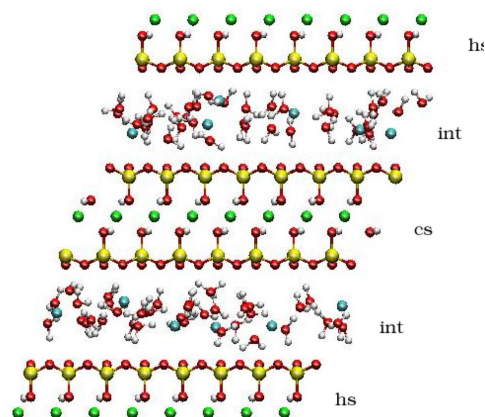
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Clays are layered aluminosilicates with water retention and ion exchange properties, which are responsible for many natural phenomena such as retention of molecules by soil and exploited in the many technological applications of clays, e.g. in catalysis and radioactive waste disposal. We deal with the microscopic structure and motion of water and cations (Na^+ and Cs^+) in clays, as a function of clay hydration. At low clay hydration, water and cations in clays are found in a quasi two-dimensional (2D) confinement between individual, negatively charged clay layers and at very high ionic concentrations (order of 10 water molecules per ion).

Using the examples of a natural montmorillonite clay and a synthetic hectorite clay we present a comparison of experimental (quasi-elastic neutron scattering) and simulated (classical Molecular Dynamics) dynamic data. These agree in the diffusion coefficient of water confined in clay, predicting its decrease by a factor of 10 and 3 with respect to bulk water, when a single and a double water layer is confined between clay layers respectively [1].

Simulation points to very different modes of diffusion for the two ions considered: a clear jump diffusion is seen between preferential adsorption sites on the clay surface for Cs^+ ions, a more diffuse motion is observed for Na^+ ions. At the same time, their diffusion coefficients are similar, of the order of $10^{-10} \text{ m}^2\text{s}^{-1}$. The 2D nature of water and ion diffusion is clearly seen in simulation, it is obscured in neutron scattering data due to the use of powder clay samples. It can be revealed, using a novel method based on analyzing the scattered intensity at zero energy transfers at a wide range of energy resolutions [2].

Lastly, we consider the exchange of ions between the interlayer, microscopic porosity of clays and a bulk aqueous solution. The calculation of the potential of mean force (PMF) for an ion entering the clay interlayer from the bulk solution reveals an energetic barrier only for negatively charged ions, supporting the experimentally observed anion exclusion from low hydrated clays [3].



Keywords: clays, confinement, water, ions, dynamics, dimensionality

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IL 29: Specificity of hydrogen bonds in protonated proton sponges and related compounds

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One of the most fascinating problems in the hydrogen bond research is the potential energy surface for the proton motion in strong, short bridges. In the present review these problems are discussed taking as examples recent results gathered for charge-assisted NHN^+ bridges in protonated proton sponges. A special attention is paid to the naphthalene proton sponges (DMAN-s) and its derivatives [1]. A variety of chemical composition of proton sponges is presented, too. In addition the resonance-assisted OHN intra-molecular bridges in liquid crystalline 2'-hydroxybenzylideneanilines and 2-hydroxyazobenzenes are discussed [2].

It was shown that NHN^+ bridges in protonated DMAN-s are characterized by IR absorption band located at very low frequencies (ca 500 cm^{-1}) assigned to the tunneling splitting. The isotopic ratio $\nu(\text{NH})/\nu(\text{ND})$ reaches high values above 2.0 that can be interpreted as due to a reversed anharmonicity [3]. A double minimum potential is evidenced by the studies of the isotope effect in the NMR spectra [4]. Even in the case of the shortest bridges such like in $\text{Si}(\text{CH}_3)_3$ 2,7-disubstituted DMAN the $\Delta\delta(^1\text{H}/^2\text{H})$ isotope effect is markedly above zero [5]. These results are in a good agreement with *ab initio* MP2 calculations.

The specific features of intramolecular $\text{OH}\cdots\text{N}$ hydrogen bonds in o-hydroxyphenyl Schiff bases are also discriminated. The properties of such bonds are particularly well reflected in IR spectra [6]. The most characteristic is the low intensity of IR bands. The discussion is presented for a number of examples and particularly for liquid crystalline o-hydroxyphenyl Schiff bases and o-hydroxyazobenzenes [2]. Based on the DFT and MP2 calculations the potential energy curves for the proton motion were analyzed [7].

Keywords: proton sponges, isotope effects, potential for the proton motion

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III Oral presentations

III.A. Basic aspect of the H-bond

Luidmil Antonov, Bulgarian Academy of Sciences, Bulgaria
"Smart Switches Based on Proton Transfer"

Oleg Filippov, Russian Academy of Sciences, Russia
"Unconventional bifurcate hydrogen bond"

Yoshiteru Matsumoto, University of Hyogo, Japan
"Hydrogen-bonded structures of Pyrrole-solvent binary clusters studied by IR cavity ringdown spectroscopy"

Majdi Hochlaf, Université Paris-Est, France.
"Photoionization and fragmentation of 2-pyridone monomer and dimer"

OP 1: Smart Switches Based on Proton Transfer

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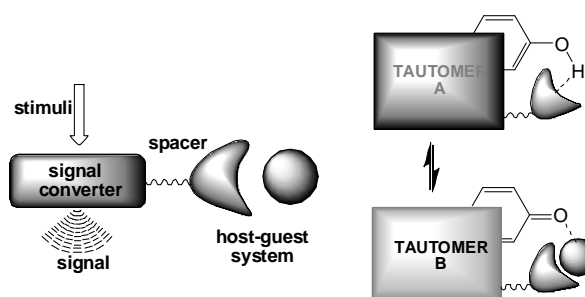
True molecular switches undergo reversible structural changes, caused by a number of influences, which give a variety of possibilities for control. A conceptual scheme of a molecular switch, based on molecular recognition, is sketched in Scheme 1. The fast and clean interconversion between structurally different molecular (on- and off-) states is the main requirement in the design of new molecular switches.

The tautomerism could be a possibility, because change in the tautomeric state can be accomplished by a fast proton transfer reaction between two or more structures, each of them with clear and different molecular properties. The conceptual idea of such device is presented in Scheme 1. In this structure, a change in tautomeric state, labeled A and B, is linked to changes in the complexation abilities of the guest-host system by modulation of the hydrogen bonding ability to the antenna. At the same time, engagement of this antenna causes a change in the tautomeric state. The sensitivity of the electronic ground- and excited states of the tautomeric forms to the environment stimuli, and to the presence of a variety of substituents or hydrogen bonding can be exploited in the design of flexible tools for control.

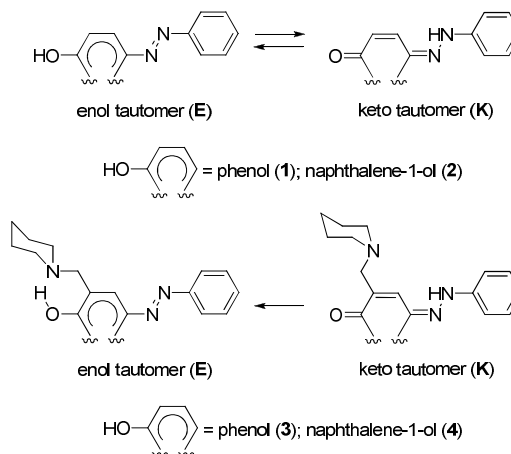
We have developed a conceptual idea for tautomeric switch, based on implementation of a flexible piperidine unit in 4-(phenyldiazenyl)naphthalen-1-ol and 4-(phenyldiazenyl)-1-phenol. The results show that a directed shift in the position of the tautomeric equilibrium can be achieved through protonation/deprotonation in a number of solvents. The developed molecular switch, in spite of the simple host-guest system, has shown acceptable complexation ability towards metal ions and can be a promising base for further development of effective molecular sensors through implementation of suitable macrocycles.

The support by The Bulgarian National Fund (Grant TK-X-1716) is acknowledged.

Keywords: tautomerism, proton transfer, hydrogen bonding



Scheme 1. Molecular switch based on molecular recognition (left) and conceptual idea for tautomerism-based molecular switch (right).



Scheme 2. Tautomeric equilibria in compounds 1-4.

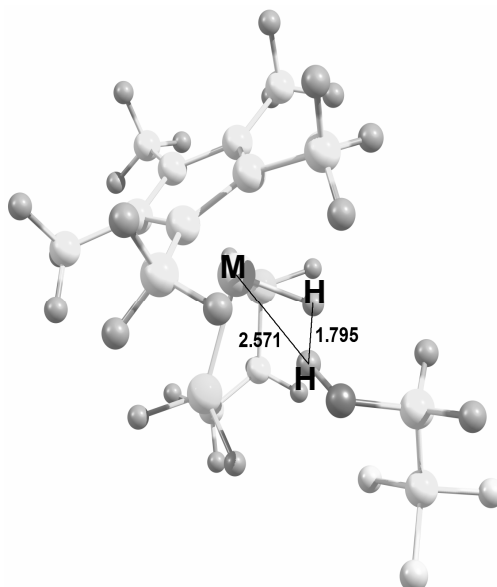
OP 2: Unconventional bifurcate hydrogen bond

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Recently found hydrogen bonds of new types: to a metal atom (XH...M) and to hydride ligand (XH...HM) are still under active investigation. These bonds are named unconventional and the last type of interaction is often called dihydrogen bond (DHB). These hydrogen bonded complexes are intermediates of proton transfer reactions playing key role in many chemical and biochemical (stoichiometric or catalytic) processes [1]. The aim of this report is to gain insight into the effect of the metal atom depending on its position in the Periodic Table on the structural and electronic characteristics of DHB complexes. We choose as the examples the hydrides of $\text{NbH}_3(\text{Cp})_2$ (V group, metal atom has no d-lone electron pairs) and Cp^*MHL (Fe, Ru, Os, VIII group, $\text{L}=\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, dppe with electron density of d-electrons increasing down the group). Experimental investigation by low temperature IR and NMR spectroscopy was combined with DFT/B3PW91 study. Spectral features of $\text{OH}\dots\text{M}$ and $\text{OH}\dots\text{HM}$ bonds will be presented.



The computational study of hydrogen bonding and proton transfer to model complexes $\text{Cp}^*\text{MH}(\text{dhpe})$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$; $\text{dhpe} = \text{H}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) was performed. The energy changes of the hydrogen bond formation are greater for the hydride than for the metal site, and the energy difference between H-complexes of two types ($\text{H}\dots\text{H}$, $\text{H}\dots\text{M}$) decreases down the group ($\text{Fe} > \text{Ru} > \text{Os}$). The analysis of DHB complexes structure and electron density distribution, indicates an asymmetric bifurcated interaction for electron rich metal (Fig.1). The impact from $\text{H}\dots\text{M}$ hydrogen bond to the total formation energy of complex increase on descending the group (5% Fe, 30% Os). The potential energy profiles for the two pathways of reaction were calculated in gas phase and solvent (CH_2Cl_2). The peculiarities of proton-transfer pathway via bifurcated HB complex, which could be expected also for other hydride complexes of electron-rich metals bearing donor ligands (for 3rd transition row), will be discussed.

Keywords: dihydrogen bonds, proton transfer, transition metal hydrides

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OP 3: Hydrogen-bonded structures of Pyrrole-solvent binary clusters studied by IR cavity ringdown spectroscopy

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Pyrrole (Py) is a heterocyclic aromatic molecule with a five-membered ring. Because Py can be considered to a building block of biological molecules, the jet-cooled Py self-aggregates and solvated clusters could provide the microscopic insight of intermolecular interactions such as hydrogen bond (H-bond) in biological systems. In order to probe the H-bond interactions, IR spectroscopy is thought to be a powerful tool. Since the NH/OH stretches are very sensitive to H-bond formations, the vibrational frequency and/or absorption intensity give us useful information concerning H-bonded structures of clusters.

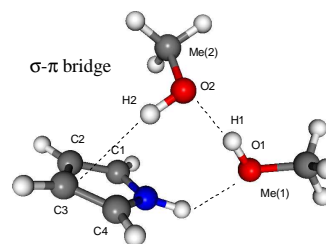
Py has two H-bond sites; one is the NH group as a donor, the other is the π electron cloud as an acceptor. Thus, we can easily expect that the Py self-aggregates have the NH- π H-bonded structures such as the T-shape in dimer and cyclic in trimer and tetramer. Recently, these structures have been confirmed experimentally by cavity ringdown [1] and FT-IR [2]. In this conference, we will present the H-bonded structures of the Py-solvent binary clusters studied by IR cavity ringdown spectroscopy (IR-CRDS).

The IR-CRD spectrometer is described in detail elsewhere [1]. The absorption intensity of vibrational transition is related to the exponential decay curve, which is the temporal pattern produced by an IR pulse leaking out of the cavity. By using the exponential decay time τ , the total round-trip loss Γ was calculated by the following equation:

$$\Gamma = 1 - \exp(-2L/c\tau),$$

where L is cavity length and c is speed of light. The absorption loss per round-trip can be obtained by subtracting the Γ in the empty cavity from that with the jet-cooled clusters. The detection limit of the absorption loss is typically 5 ppm in our apparatus.

For the Py-solvent 1:1 clusters with H₂O, CH₃OH, and C₂H₅OH, the observed NH stretches of Py site were red-shifted by 80 – 120 cm⁻¹ from that of monomer, which indicates the NH-O type H-bond formation in 1:1 clusters. For the Py-(CH₃OH)₂ cluster, we observed two bands at 3432 and 3549 cm⁻¹, which were assigned to the OH and/or OH-containing stretches. The MP2 calculation revealed there are several isomers in 1:2 clusters. Among them, only the σ - π bridge H-bonded structure has the $\nu_{\text{NH}} \pm \nu_{\text{OH}}$ vibrations at ~3440 cm⁻¹. Thus, we concluded that the 1:2 cluster has the σ - π bridge structure such as NH-OH-OH- π electron cloud [3].



Keywords: pyrrole, solvated clusters, IR cavity ringdown spectroscopy, σ - π bridge structure

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OP 4: Photoionization and fragmentation of 2-pyridone monomer and dimer

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The 2-pyridone, its dimer as well as their charged species are systems model to study the DNA bases, isolated or paired, as well as the hydrogen bonding in their complexes. Several experimental and theoretical studies of the neutral molecule (2-pyridone) exist [1-6]. This work concerns the experimental treatment of biological small weakly bound complexes in the gas phase and their dynamics, together with a close interaction with theoretical *ab initio* calculations on these species. We considered the photoionization of the 2-pyridone monomer, its tautomer and its dimer, as a first step for studying the DNA nucleobases and their homologues. These studies should help our understanding on the pairing processes between these nucleobases, their structures, the mechanisms of their photoionization and the reaction pathways undertaken when proton transfer is occurring there. Fundamental quantities, such as ionization energies, dissociation energies and binding energies of these species are determined accurately.

Recent state-of-the-art computations dealing with the 2-pyridone cation showed the high density of the electronic states of the cation for internal energies 4-8 eV [7]. Hence, these electronic states are mutually coupled vibronically and via spin-orbit interactions. In addition to the investigation of the structure and the spectroscopy of these electronic states, our experimental data give insight into the nature of these couplings and their efficiency as we already shown for other molecular systems. Besides, proton loss channel is lying in the 4-8 eV energy range. The dissociation of 2-pyridone along this channel involves several electronic states and their mutual couplings. Finally, we think that intramolecular rearrangements of our ionic system (lactam form), such as the isomerization into his isoenergetic form tautomer (Lactim form), are likely to occur during or after ionization and to lead to other dissociation products. These dissociation channels are located much lower in energy than the proton loss asymptote. These dissociations are investigated through the study of the fragmentation of the cation.

Similar studies are performed on the 2-pyridone dimer. The data on the monomer and the dimer allow deducing an accurate value for the binding energy in the dimer and hence a good estimation of the hydrogen bond energy (= half of the binding energy of the dimer since the dimer possesses two hydrogen bonds). More interestingly, the binding energy in the cationic dimer is found to be about 3 eV i.e. much larger than two hydrogen bond energies. In the cationic dimer, electron transfer is occurring from one monomer to another resulting the formation of H bridged bounds instead of the H bonds. This is the first time that such effect is observed.

We will focus our presentation on the study of the photoionization of the 2-pyridone, and its dimer, according to the recent state-of-the-art theoretical data dealing with the electronic structure of the 2-pyridone cation, its intramolecular isomerization and decomposition [7]. In the future and once the methodology is established, the DNA bases will be treated. The experimental work is done using the new Threshold PhotoElectron PhotoIon Coincidence (TPEPICO) spectrometer installed at the DESIRS beamline in Synchrotron SOLEIL. For studying the fragmentation of this cation after its formation, we measured the threshold electrons and the ions coming from the same event in coincidence. Our theoretical data are done using configuration interaction and TD DFT methodologies.

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III.B. Small Bulding blocks

Alfred Laubereau, Physik-Department, Technische Universitaet Muenchen, Germany
"Hydrogen Bonds in Solid Hydrates of Aqueous Salts studied by Quantum Simulations and Subpicosecond Infrared Spectroscopy"

Michael Odelius, Department of Physics, Stockholm University, Sweden
"Probing hydrogen bonds with x-ray emission spectroscopy"

Peter M Tolstoy, Institut für Chemie and Biochemie, Freie Universität Berlin, Germany
" UVNMR Study of Proton Tautomerism in Strong Anionic OHO Hydrogen Bonds "

OP 5: Hydrogen Bonds in Solid Hydrates of Aqueous Salts studied by Quantum Simulations and Subpicosecond Infrared Spectroscopy

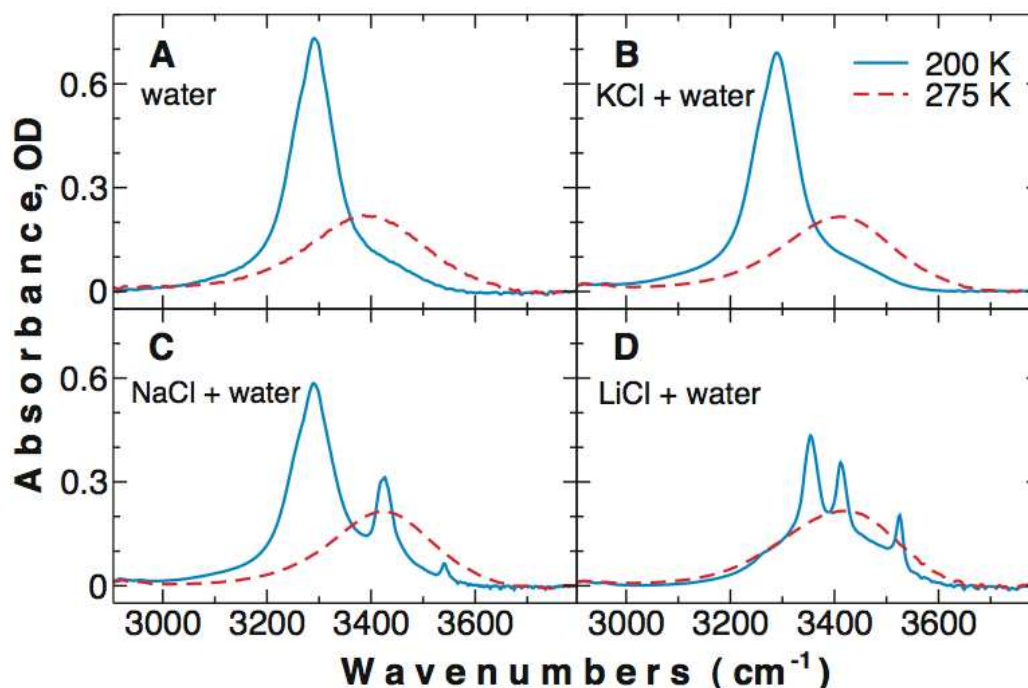
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We report on the structure and vibrational spectra of aqueous alkali chlorides in the crystalline phase using a combination of experimental and theoretical techniques. The spectra were computed from Born-Oppenheimer molecular dynamics (BOMD) simulations within the density functional theory (DFT) framework as well as simulations with newly developed force fields that are fit to high level electronic structure results for the ion-water and water-water interactions.^{1,2} The agreement of the theoretical results with conventional FTIR data demonstrates the progress achieved in the description of the underlying molecular interactions and their dynamics and allows for the correspondence of the narrow absorption OH-bands of the solid hydrates in HOD:D₂O mixtures with well-defined structures of the hydrogen-bond environment. Some FTIR spectra are shown below. Special emphasis is given to the NaCl dihydrate, where also a time-resolved study was carried out using two-color IR spectroscopy. The water molecules bound in that hydrate show two well separated absorption bands of the OH-stretching mode of HOD at 3426 cm⁻¹ and 3541 cm⁻¹. After excitation of the OH stretching vibration the relaxation and ultrafast heating of the polycrystalline ice-hydrate was investigated. For the lower-frequency OH band of HOD the population lifetime of in the NaCl hydrate is measured to be 6.8 ± 1 ps, significantly larger than for neat water. Our recent computational and experimental results demonstrate the potential of aqueous hydrates for an improved understanding of hydrogen-bonded environments.



Keywords: hydrates, intermolecular interactions, hydrogen bonding, time-resolved spectroscopy

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OP 6: Probing hydrogen bonds with x-ray emission spectroscopy

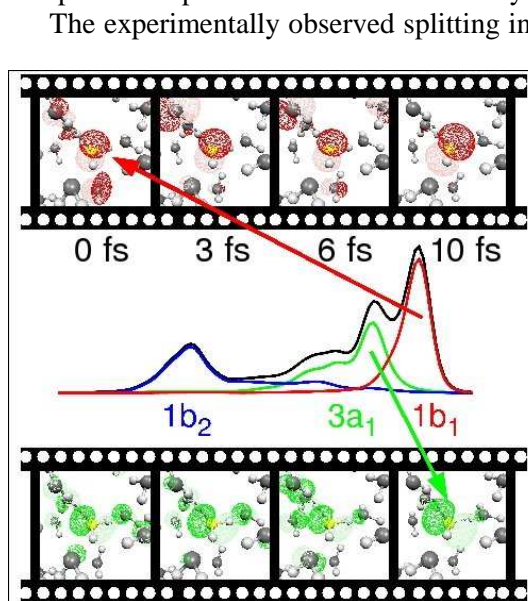
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Does the fine-structure in oxygen K-edge x-ray emission imply that liquid water is a two-component mixture or is it the signature of a transient OH species arising in the core-excitation process?

X-ray spectroscopy can be used to probe the local electronic structure and gain information on molecular structure and chemical bonding. Hence, it is an ideal tool for use in time-resolved pump-probe spectroscopy to follow the molecular dynamics and changes in chemical bonding in ultra-fast photo-induced processes. The core-hole decay allow us to consider x-ray emission (XE) as pump-probe experiment with an inherent time-scale of 0-10 femtoseconds. By combining ab initio molecular dynamics and spectrum simulations to interpret the experimental data we can study ultra-fast dissociation in water [1].



The experimentally observed splitting in the lone-pair peak in x-ray emission is reproduced on the basis of ab initio molecular dynamics simulations [2]. The difference in angular anisotropy in the water lone-pair features is related to their fundamentally different origin [3]. The high emission-energy peak is primarily due to the contribution from the out-of-plane ($1b_1$) lone-pair in intact water molecules. The low emission energy lone-pair peak, on the other hand, originates from the bonding ($3a_1$) state and is assigned to a transient OH species formed by ultra-fast (<10 femtoseconds) photo-dissociation. The information in the XE spectrum on the structure of hydrogen bonded liquids, such as water, is limited and buried in features arising from excited state dynamics. Time-resolved spectroscopy to probe electronic structure goes beyond traditional laser pump-probe experiments in that many aspects of the electronic structure can be directly probed, but the richness in the spectroscopic data creates a heavy dependence on a theoretical counterpart.

The spectroscopic probes are naturally linked to electronic structure calculations, which form a rich basis for interpretation of the spectral data. The studies on liquids are put in contrast to time-resolved vacuum-ultraviolet photo-electron spectroscopy on isolated molecules, for which high level theory can be afforded. We show how valence orbitals evolve during dissociation from a diatomic molecule to the free atoms, by mapping the evolution of the entire occupied valence electronic structure during photo-dissociation of Br_2 molecules [4].

Keywords: ab initio molecular dynamics simulations, x-ray spectroscopy, ultra-fast dynamics

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OP 7: UVNMR Study of Proton Tautomerism in Strong Anionic OHO Hydrogen Bonds

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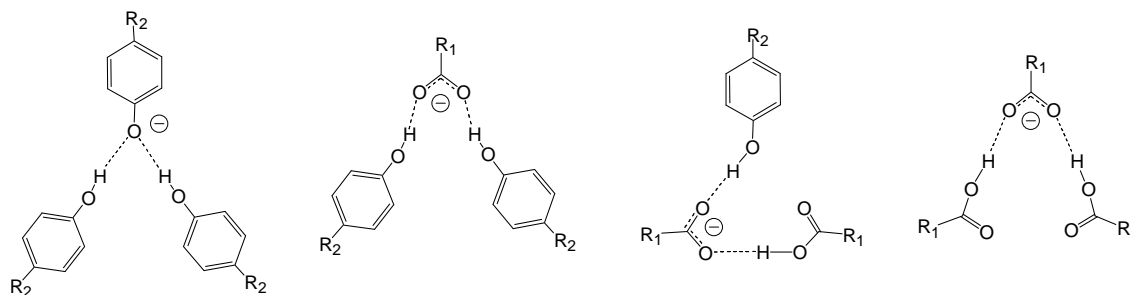
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Intermolecular complexes with one or several short anionic hydrogen bonds often exhibit proton tautomerism between several equilibrium structures. Lifetimes of tautomers are usually in the range from nano- to microseconds and thus signals from proton tautomers are not resolved in NMR spectra. To obtain the information about individual tautomers we have recently proposed to use a setup for combined NMR and UV-Vis measurements (UVNMR) [1]. In this method the information which can be derived from the averaged NMR signals ("fast exchange regime") is supplemented by the simultaneously measured UV-Vis spectra, for which proton tautomers are in the "slow exchange regime".

In this work we present our UVNMR study of a series of intermolecular anionic complexes with strong OHO hydrogen bonds formed between nitrophenolate and carboxylate residues in polar aprotic solvents, CD_2Cl_2 and $\text{CDF}_3/\text{CDF}_2\text{Cl}$. Investigation of 1:1 complexes with isolated hydrogen bonds allowed us to establish correlations between spectroscopic observables (^1H , ^{13}C chemical shifts, H/D isotope effects on them, wavelength of the UV-Vis band maximum) and H-bond geometry. These correlations are applied to the complexes with several coupled hydrogen bonds (see the Figure). Some of these complexes exist in a single form, while others display fast dynamic processes, involving proton transfers and hydrogen bond flips. The cause of this tautomerism and the effects of the polar aprotic medium on the structure of individual tautomers are discussed.



Keywords: UVNMR, Coupled H-bonds, H/D Isotope Effects, H-Bond Correlations

[1] P. M. Tolstoy, B. Koeppel, et al, *Angew. Chem.* 2009, DOI: 10.1002/anie.200806181.

III.C. Materials 1

Hiroshi Fukazawa, Neutron Materials Research Center, Japan Atomic Energy Agency, Japan
"Properties of ferroelectric and hydrogen ordered ices in space"

Giovanni Strazzulla, INAF-Osservatorio Astrofisico di Catania, Italy
"H bonds in astrophysical ices"

Oliver Kühn, Institute of Physics, Germany
"Two-Dimensional Infrared Spectroscopy of the Correlated Dynamics of the Adenine: Uracil Hydrogen Bonds in CDCl₃ Solution"

Virginie Marry, Université Pierre et Marie Curie - Paris 6, France
"H-Bond network in clays from molecular simulations"

Patrick Judeinstein, Université Paris-Sud 11, France
"Structure and Dynamics of Protic Ionic Liquid: NMR and neutron studies"

Valentina Venuti, Department of Physics, University of Messina, Italy
"T-dependence of the vibrational dynamics of IBP/ β -CDs inclusion complexes by FTIR-ATR spectroscopy and numerical simulation"

François-Xavier Coudert, Chimie ParisTech, France
"Water Nanodroplets Confined in Zeolite Pores: Quantifying the Strength of Hydrogen Bonds from Simulation"

Esben Ravn Andresen, Physicalisch-Chemisches Institut, Universität Zürich, Switzerland
"Nonlinear infrared pump-probe spectroscopy on a metal hydride: Insight into the ultrafast dynamics and the potential-energy surface"

Martina Roeselová, Institute of Organic Chemistry and Biochemistry ASCR, Czech Republic
"Hydrogen bonding in nanodroplets and thin water films on functionalized self-assembled monolayers"

OP 8: Properties of ferroelectric and hydrogen ordered ices in space

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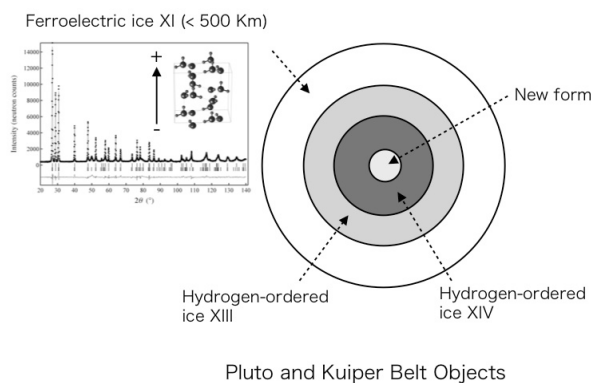
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In the Galaxy, ice is one of the major solid components in a low-temperature environment. Ice crystal has been identified by infrared spectra in interstellar molecular clouds. Icy grains broadly exist in the early solar system. The main ingredient of planets beyond Jupiter is ice. The icy grains grow and become big icy bodies, such as Pluto and Charon.

The nucleation and growth of ferroelectric ice, named ice XI (eleven), has been studied by time-resolved neutron diffraction experiments on High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory. The study shows that the hydrogen in ice is slowly ordered at 55 - 70 K and the resulting solid becomes ferroelectric [1,2].

The properties of ferroelectric ice are of interest in space because of long-range electrostatic force. The strong electrostatic force promotes the growth and agglomeration of icy grains. Furthermore, ferroelectric ice captures a number of electrons and ions in space. These properties of ice may have an important role for planetary formation and material evolution.

In this conference I report recent neutron diffraction studies and preliminary results of hydrogen-ordered ices under high pressure. The ferroelectric ice and hydrogen-ordered ices are stable in wide range of temperature and pressure. Therefore it is estimated that a large amount of hydrogen-ordered ice exists in our solar system. We have measured infrared absorption spectra of those ices. Our results demonstrate that the ordered ices in space are detectable using infrared telescope and planetary exploration. I discuss a whole picture of water ice in a low-temperature environment.



Keywords: water, ice, neutron, planet

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OP 9: H bonds in astrophysical ices

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The mid-infrared spectrum of amorphous solid water (ASW) shows a number of absorption bands, among which one at about 3300 cm^{-1} due to the O–H symmetric and anti-symmetric stretching modes. The peak position of the stretching modes is sensitively different from the one observed in gas phase water molecules. Each water molecule is in fact glued by covalent O-H bond. In the solid (or liquid phase) the H-bond occurring between the H atom of a molecule with the O atom of a different molecule causes a shift of the O-H stretching band. This simple fact permitted, since the 70's of last century, to observe the O-H stretching band in the ground based IR spectra of many astrophysical objects [1] otherwise inhibited by the presence of abundant water vapor in the Earth atmosphere. Those observations opened the era for a new chapter of astrophysical research, that on the frozen gases (ices) present in several astrophysical environments as e.g. icy mantles on interstellar and circumstellar dust grains, and on large solid objects in the Solar System.

In the spectrum of ASW, a small feature is present on the long wavenumber wing of the O–H stretching modes band, due to OH dangling bonds (db) in the micropores of the amorphous structure. The profile of the OH dangling bond feature (peak position and shape) depends on the temperature and on the presence of other species mixed in with water ice. Here we present IR spectra obtained at low T (15-150 K) after the co-deposition of several mixtures of H₂O with other species (e.g., CO, CO₂, N₂, CH₄, SO₂, etc) [2].

This db feature can be considered as due to a "lacking H-bond". When a molecule is frozen in a mixture with water (e.g. CO) a bond can be formed with the dangling OH [3]. This causes both the shifting of the peak position of the db feature and the appearance of a band at 2152 cm^{-1} which is assigned to CO bonded to the dangling OH groups [4].

Although water ice mixed with other molecules has nowadays been observed in a plethora of environments, no features attributed to OH dangling bonds or to the interaction of host molecules with dangling OH have been reported so far [5]. This would imply that the observed amorphous ices are in fact compact (i.e. no db are present in the disordered structure). It has been suggested that energetic processing (radiolysis and photolysis) of astrophysical ice causes its compaction. We have studied such processes in the laboratory and we have found that after processing the bands due to the O–H dangling bonds are in fact reduced in intensity and eventually disappear [2,6].

Keywords: ice, radiolysis

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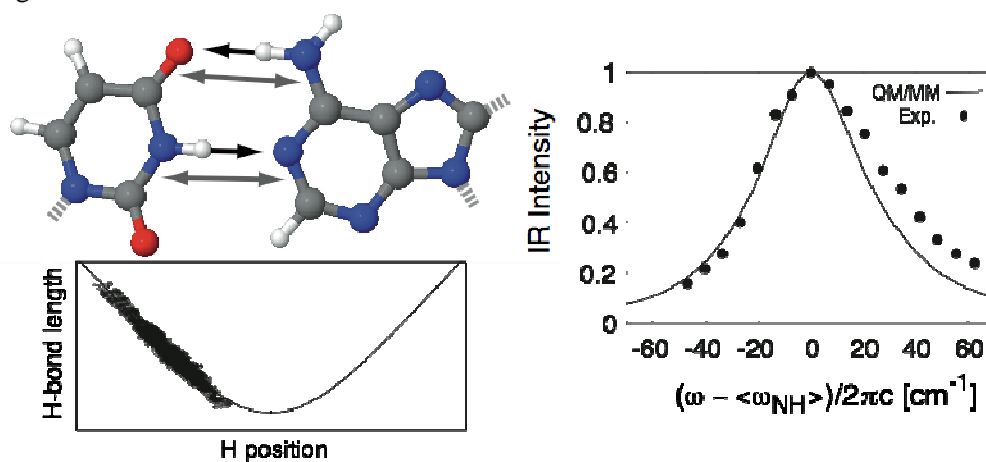
OP 10: Two-Dimensional Infrared Spectroscopy of the Correlated Dynamics of the Adenine: Uracil Hydrogen Bonds in $CDCl_3$ Solution

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Hybrid QM/MM molecular dynamics simulations have been carried out for the Watson-Crick base pair of 9-ethyl-8-phenyladenine and 1-cyclohexyluracil in deuteriochloroform solution at room temperature [1,2]. Trajectories are analysed putting special attention to the geometric correlations of the N-H...N and N-H...O hydrogen bonds in the base pair. Even though the two hydrogen bonds are only approximately linear and the heterocycles are tilted with respect to each other, hydrogen bond and N-H lengths follow a simple empirical correlation based Pauling's valence bond order model.



In order to describe the IR line shape of the two NH stretching vibrations, the correlation between their fundamental transition frequencies and the hydrogen bond lengths is exploited. This facilitates efficient determination of the fluctuating transition frequencies along the QM/MM trajectory. Using IR line shape theory, the fundamental NH stretching transitions are obtained to deviate by less than 2% from the experimental values obtained by Woutersen and Cristalli [3]. Analysis of the frequency correlation functions is shown to provide insight into anharmonic couplings to low-frequency modes that are responsible for the line broadening.

Finally, the line shape function is used to explore the correlated dynamics of the two hydrogen bonds on the basis of the two-dimensional IR spectrum.

Keywords: IR spectroscopy, base pairs, QM/MM

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OP 11: H-Bond network in clays from molecular simulations

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Clays are layered alumino-silicate minerals which are involved in many industrial and environmental processes. They are used as multi-barrier systems for retaining pollutants. Water of soils in contact with clays is responsible for the swelling of clays and is linked to their properties of adhesion and plasticity. It is also the fluid which can be the vector of the motion of hazardous elements. In particular, water at the surface of clays determines the hydrodynamic properties of flows through the interlayer, interparticle and macroscopic porosities.

Molecular simulations can provide information on water properties at the microscopic scale. We show that the existence of preferential sites on the clay surface leads to specific hydrogen bonds patterns which slow down the dynamics along and perpendicular to the clay surfaces. In the first molecular layer near the surface approximately half of the water molecules are H-bonded to the surface. We also analyze the H-bond network between surface water molecules. The basal surface H-bonds formation and dissociation dynamics can be described by a simple kinetic model to allow the comparison with bulk water dynamics. It suggests that formation is faster with the surface than in the bulk, while H-bond dissociation is slower.

Keywords: montmorillonite, clay, water, molecular dynamics, diffusion

OP 12: Structure and Dynamics of Protic Ionic Liquid: NMR and neutron studies

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Polymer Exchange Membrane Fuel Cells (PEMFCs) are expected to fulfil many promising applications as power sources. The heart of such systems is the electrolyte membrane which should provide sufficient protonic conduction in adequation with the operating conditions. Perfluorinated Nafion[®] membranes are often considered as promising candidates, however, their protonic conductivity involves water molecules entrapped inside the membranes and then the main drawback is the upper limit temperature which is around 80°C.

To circumvent such issue, anhydrous protonic conductivity is required and Proton Conducting Ionic Liquids (PCIL) were developed to reach high degree of protonic conductivity even in anhydrous conditions. In this work, we focus on a family of protic ionic liquid synthesized by reacting alkylamine with various acids.^{1,2} Membranes with high conductivity are obtained when Nafion[®] foils are swollen by these PCILs.²

However, the conductivity and stability of these membranes are strongly related to the intimate structure of the ionic liquid component, more especially the nature of the proton charge carrier (bare H⁺ vs. ammonium) and ionic dissociation.

This paper reports on studies of the local structural organization of these PCILs as well as on the dynamic of the different counterparts. Combination of various nuclear magnetic resonance (NMR) experiments and Quasi-Elastic Neutron Scattering (QENS) allow to decipher structure and dynamics of these intriguing liquids in the *pm-μm* space and *pico-* to *second* scales :

- NMR scalar correlations and intermolecular Overhauser spectroscopies (¹³C, ¹H and ¹⁵N, ¹H) experiments probe the nature of protonic species and ion-pairing;
- QENS yields elementary mobility steps at the molecular level while pulsed field gradient NMR measure the long range (*μm*) translational self diffusion coefficient of all the PCIL components as well as concerted translational motions.

These techniques point out some strong ion-ion interactions which are based on hydrogen bonding and explains the unusual properties of such liquids.

Keywords: protic ionic liquid, NMR, QENS

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OP 13: T-dependence of the vibrational dynamics of IBP/ β -CDs inclusion complexes by FTIR-ATR spectroscopy and numerical simulation

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Inclusion, or host-guest, complexes are supramolecular assemblies in which two or more molecules hold together and organize by means of intermolecular non-covalent bonds. The study of the mechanisms occurring in the formation of supramolecular assemblies is a topic of current interest in physical chemistry. Examples of supramolecular systems include biological membranes, polynuclear metal complexes, liquid and molecule-based crystals. Even cells can be envisaged as very complex supramolecular systems, where assemblies involving nucleic acids and proteins are studied.

As host molecules, unsubstituted and derivative β -cyclodextrins (β -CDs) are probably the most important example of relatively-simple organic compounds exhibiting inclusion complex formation with a variety of organic guest molecules, thereby altering the chemical and physical properties of the latter [1-3]. Pharmaceutical applications of β -CDs are widespread, mainly for their effectiveness in improving the water solubility, chemical stability and bioavailability of various hydrophobic drugs.

FTIR-ATR spectroscopy has been used, in solid phase, to monitor the changes induced, as a consequence of complexation in β -cyclodextrin (β -CD), (2-hydroxypropyl)- β -cyclodextrin (HP- β -CD) and methyl- β -cyclodextrin (Me- β -CD), on the vibrational spectrum of the non-steroidal anti-inflammatory drug Ibuprofen (IBP, (2-[4-(2-methylpropyl)phenyl]-propanoic acid). The evolution of the spectral modifications has been followed as a function of temperature from 220 to 340 K, in the wavenumber range 600 \div 4000 cm⁻¹. At the same time, quantum chemical calculations were performed on monomeric and dimeric structures of IBP, derived from symmetric hydrogen bonding of the two carboxylic groups, in order to unambiguously assign some characteristic IR band in IBP spectrum. The comparative analysis of the results obtained by this experimental-numerical approach allowed us to evaluate the average height of the energy barrier which must be exceeded in order to observe a complexation event between one molecule of IBP and one of CD.

Keywords: Inclusion complexes, FTIR-ATR spectroscopy, numerical simulation.

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OP 14: Water Nanodroplets Confined in Zeolite Pores: Quantifying the Strength of Hydrogen Bonds from Simulation

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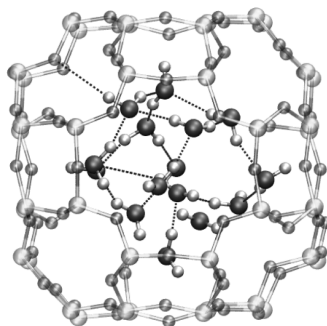
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The confinement of a fluid to spaces of molecular dimensions, such as a nanoporous material, triggers important changes in its physical and chemical properties. The role of confinement is a key to understanding the behaviour of many systems, ranging from biological membranes to nanoporous materials used in the oil industry.

We have studied the behaviour of liquid water adsorbed inside the small, 3D-connected cavities of zeolites A with varying chemical composition and acidity. The influence of the confinement on the physical and chemical properties of the water was characterized by calculating and analyzing a wide range of properties, going from electronic structure (distribution of water dipole moment, atomic polarisability tensors) to the structure and dynamics of the hydrogen bonds network. This very wide range of problems has been addressed by the use of two different techniques: first principles Car-Parrinello molecular dynamics and molecular dynamics using carefully crafted classical interaction potentials with the host material.

We have demonstrated the formation of nanodroplets of 15 to 20 water molecules (~ 1 nm in diameter), whose dynamics resemble that of bulk liquid water. The direct calculation of the confined water infrared spectrum (this is, to our knowledge, the first direct ab initio calculation of the IR spectrum of water near an interface) exhibits a clear peak at high frequencies.¹ Further analysis confirmed it to be due to non hydrogen-bonded, dangling OH groups (oriented toward the interface). The absence of water-zeolite hydrogen bonds was further demonstrated by analysing the atomic polarisability tensors of hydrogen atoms, which are a clear signature of hydrogen bonding. When the acidity of the zeolite is increased, it becomes hydrophilic and we have shown that this change goes together with the existence of water-zeolite hydrogen bonds of increasing strength and lifetime.² We have also shown how the dynamics of the hydrogen bonds network is modified from that of the bulk, using a recent model from Hynes and Laage³; we show that while the dynamics of the water reorientation is significantly slowed, the mechanism of the switch in hydrogen bond partner follows the same mechanism as in bulk water.



Keywords: water, confinement, molecular simulation

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OP 15: Nonlinear infrared pump-probe spectroscopy on a metal hydride: Insight into the ultrafast dynamics and the potential-energy surface

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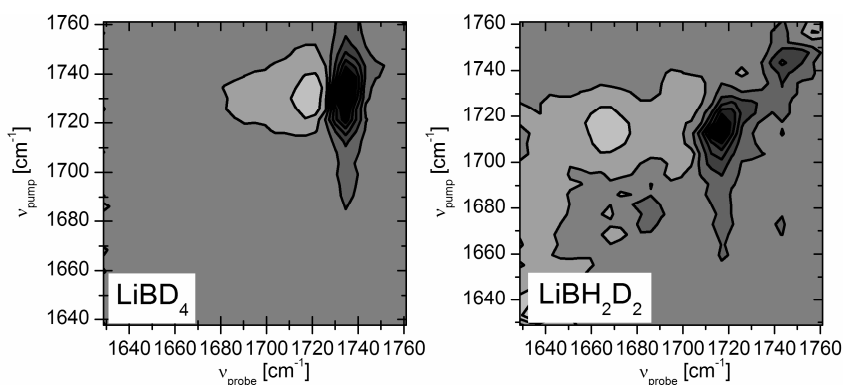
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Tetrahydroborates represent a class of complex hydrides with the largest gravimetric hydrogen density [1]. Therefore, these compounds are potential hydrogen storage materials for mobile applications. Nevertheless, hydrogen release and uptake only occurs at pressures and temperatures, which are unpractical for realistic applications. A fundamental, microscopic understanding of the B-H bond and its interactions could yield valuable understanding to relate the microscopic to the macroscopic parameters [2].

We study the tetrahydroborate LiBH_4 and its isotopomers LiBH_3D , LiBH_2D_2 , LiBHD_3 , and LiBD_4 in equilibrium in the low-temperature phase, focusing on the B-X (X = H,D) vibrations employing spectroscopic methods based on ultrafast lasers, namely infrared pump-probe (IR-pp) and 2-dimensional infrared (2DIR) spectroscopy. IR-pp spectra reports on vibrational lifetimes of the B-H and B-D vibrations, found to be universally 1.5 ps. They also carry the spectroscopic signature of the thermalization after excitation by the IR-pump pulse. A temperature increase of 6 K and a timeconstant for thermalization of 3 ps are found, although full thermalization does not occur until several 100 ps. 2D-IR spectra report on the anharmonicity and hence the shape of the potential. We find that anharmonicities are markedly larger in isotopically substituted unit cells than in the pure hydrides and deuterides.

IR-pp and 2D-IR spectroscopy probe parameters that are inaccessible otherwise and the IR-pump pulse, due to the ultrafast temperature jump it induces, could be used as an ultrafast trigger for the microscopic study of phase transitions.



Keywords: LiBH_4 , anharmonicity, DFT, infrared spectroscopy, ultrafast, vibrational dynamics

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OP 16: Hydrogen bonding in nanodroplets and thin water films on functionalized self-assembled monolayers

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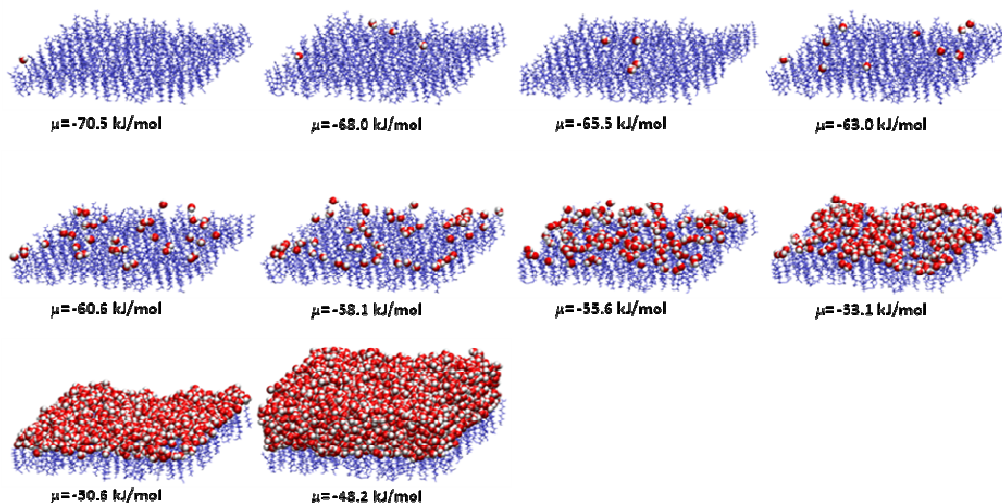
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Under ambient conditions, most surfaces are coated by a thin film of water, which controls important physico-chemical processes, from adhesion and lubrication to wear on paintings and buildings to aerosol or cloud droplet nucleation, to name just a few examples. Yet despite their importance in many fields, a molecular level understanding of the properties of thin water films is largely missing.

In our recent studies[1,2], we used molecular dynamics (MD) simulations with constant number of molecules to study the evolution of the structure and hydrogen bonding of water molecules on the flat surface of well-ordered self-assembled monolayers (SAMs) of eight carbon alkanethiol chains bound to a gold substrate, as the character of the surface was finely tuned from completely hydrophobic to completely hydrophilic, and as the level of hydration was increased from sub-monolayer to the equivalent of about two monolayers of water. The hydrophilicity of the SAM surfaces was increased by randomly replacing methyl (CH₃) terminated alkanethiol chains with carboxylic acid (COOH) terminated chains.

More recently, we have extended this study also to CH₃/OH mixed SAMs. In addition, we have employed the Grand Canonical Monte Carlo (GCMC) approach to answer the more quantitative questions, such as: How much water can be taken up by various surfaces? What is the role of chemical functionality vs. surface roughness in controlling water uptake? How many molecular layers make up the thin film at different relative humidity of the atmosphere? The results provide important insight into the structure and hydrogen-bonding of varying amounts of water on heterogeneous organic surfaces exposed to the atmosphere at varying relative humidity.



Keywords: molecular dynamics, Grand Canonical Monte Carlo, microscopic wetting

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III.D. Biological systems

Daniela Russo, Institut Laue Langevin, France

"Water hydrogen bond analysis on hydrophilic and hydrophobic bio-molecules sites"

Damien Laage, Ecole Normale Supérieure, France

"Why water reorientation slows down without iceberg formation around hydrophobic solutes"

Paul R. Tulip, University of Edinburgh, UK

"Peptide aggregation and solvent electrostriction in a simple model dipeptide via molecular dynamics simulation"

David R. Nutt, University of Reading, UK

"A dual functional role for the solvation shell of an insect antifreeze protein"

Barbara Rossi, University of Trento, Italy

"Micro-structural investigation of SOUL protein single crystals by Raman scattering experiments and numerical simulation"

OP 17: Water hydrogen bond analysis on hydrophilic and hydrophobic biomolecules sites

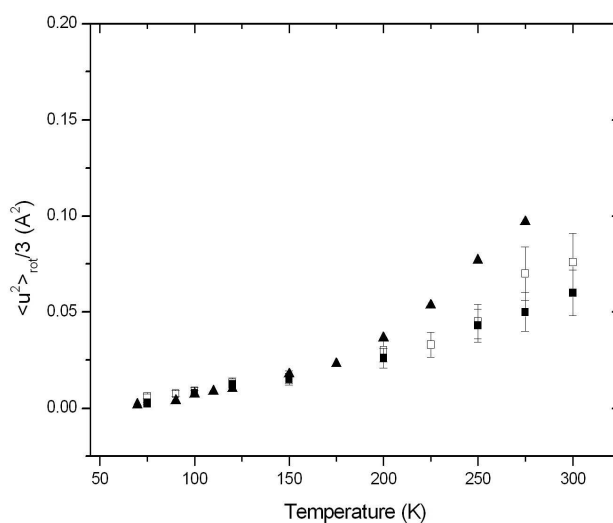
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Elastic and quasielastic neutron scattering experiments have been used to investigate the hydrogen bonding network dynamics of hydration water on hydrophilic and hydrophobic sites. The results suggest that the dynamical contribution of the intrinsic and low hydration molecules of water is characteristic of pure librational/rotational movement. The water molecule remains attached to the hydrophilic site with the only possibility of hindered rotations that eventually break the bond with the peptide and reform it immediately after. A gradual evolution from librational motions to hindered rotations is observed as a function of temperature. When the hydration increases we observe, together to the hindered rotations of hydrogen bonds, a slow diffusion of water molecules on the surface of the peptides.



Mean square fluctuations $\langle u^2 \rangle/3$ plotted as a function of temperature for hydrated d-NALMA (10% filled square, 30% open squares) and hydrated d-NAGMA (30% filled triangle)

OP 18: Why water reorientation slows down without iceberg formation around hydrophobic solutes

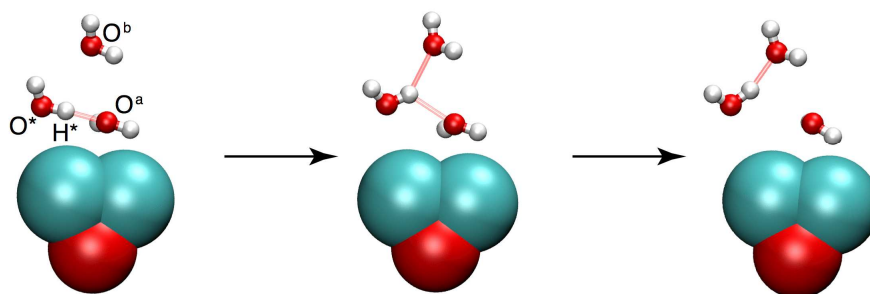
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The dynamics of water molecules next to hydrophobic solutes is investigated, specifically addressing the recent controversy raised by the first time-resolved observations¹, which concluded that some water molecules are immobilized by hydrophobic groups, in strong contrast to NMR² and simulations conclusions. Through molecular dynamics simulations and an analytic jump reorientation model, we identify the water reorientation mechanism next to a hydrophobic solute and evidence that no water molecules are immobilized by hydrophobic solutes¹. Their moderate rotational slowdown compared to bulk water (e.g. by a factor of less than two at low solute concentration) is mainly due to a slower hydrogen-bond exchange. The slowdown is quantitatively described by a solute excluded volume effect at the transition state for the key hydrogen-bond exchange in the reorientation mechanism. We show that this picture is consistent with both ultrafast anisotropy¹ and NMR² experimental results, and that the transition state excluded volume theory yields quantitative predictions of the rotational slowdown for diverse hydrophobic solutes of varying size and over a wide concentration range³. We also explain why hydrophobic groups slow water reorientation less than do some hydrophilic groups. The spectral behavior of the water molecules in the vicinity of hydrophobic groups is investigated through the calculation of two-dimensional infrared spectra and frequency-frequency time correlation functions.



Keywords: water reorientation, hydrophobic

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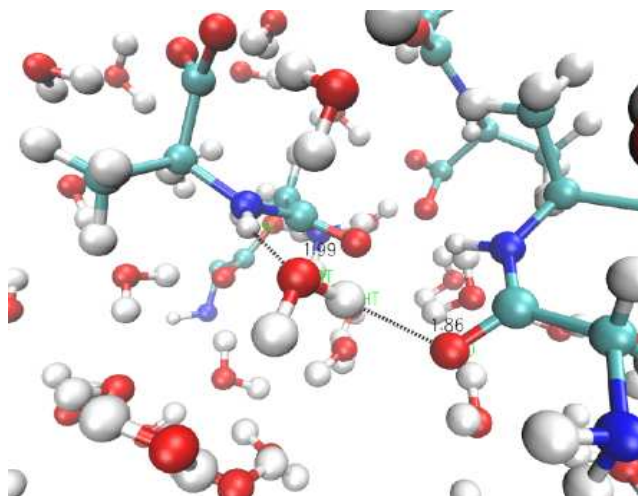
OP 19: Peptide aggregation and solvent electrostriction in a simple model dipeptide via molecular dynamics simulation

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We investigate the structure of the glycyl-L-alanine dipeptide in aqueous solution at a 1:20 peptide:water concentration via classical, atomistic molecular dynamics simulations using the CHARMM22 force field, and compare to recent neutron diffraction data [1,2]. Comparison between simulations and experiments is made using the static structure factor $S(Q)$. The effect of water model (TIP3P, TIP4P and SPC/E) upon the solution structure is investigated. Agreement between experiment and simulation is generally good across the entire Q range, although some model-dependent variation is observed, particularly in the predicted intensities of features in $S(Q)$. Peptide aggregation is found to be driven by "hydrophilic" (often bifurcated) hydrogen bonds between carboxy and amine functional groups, although simulations suggest that the degree of aggregation is less than that observed experimentally. Detailed examination of the solute structural motifs reveals the existence of bifurcated motifs that are suggested to be an artifact of the CHARMM force field, and may imply that classical force fields provide a flawed structural and dynamical description of such molecular fluids. Investigation of the water structure reveals the presence of an electrostrictive effect that manifests itself as an increase in the number of interstitial molecules in the water second coordination shell, in contradiction to suggestions that this phenomenon arises owing to hydrogen bond bending. Examination of the solvation structure suggests that the CHARMM force field overhydrates the terminal carboxy group, and that this overhydration is accompanied by the presence of bifurcated hydrogen bonds.



Keywords: Peptides, molecular dynamics, neutron diffraction

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OP 20: A dual functional role for the solvation shell of an insect antifreeze protein

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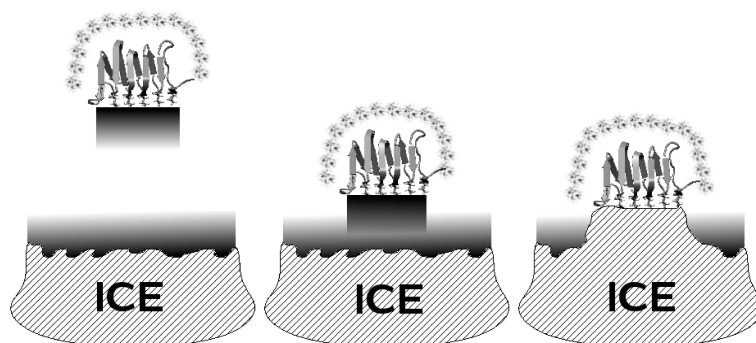
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Antifreeze proteins are found in insects and fish which inhabit cold environments and function by recognising and binding to the surface of small ice crystals, thereby preventing further growth. In many cases, the putative ice-binding face(s) of these small proteins have been identified by mutation studies and molecular modeling. Based on results from mutagenesis experiments and simulations, it has previously been suggested that the protein itself assists in the formation of the ice surface[1], a hypothesis strengthened by the observation of structural water molecules at the ice-binding surface of the protein in X-ray structures of antifreeze proteins from insects[2]. If this is the case, additional structuring of (liquid) water would be expected around the ice-binding site of the protein in solution.

Using atomistic molecular dynamics simulations of antifreeze proteins in (liquid) water and at the ice-water interface, we have investigated the structure and dynamics of the protein solvation shell. Results indicate that the protein hydration shell plays two different functional roles. Firstly, increased water ordering around the ice-binding face of the protein reduces the entropic cost of the irreversible binding to the ice surface required for antifreeze activity. Secondly, disruption of water structure around the rest of the protein helps prevent further ice growth[3].



Keywords: protein hydration, ice, molecular dynamics simulations

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OP 21: Micro-structural investigation of SOUL protein single crystals by Raman scattering experiments and numerical simulation

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Protein SOUL is a new member of the recently discovered putative heme-binding protein family called SOUL/HEBP and to date, no structural information exists for this protein. Here, micro-Raman spectroscopy is used to study the vibrational properties of single crystals obtained from wild-type protein SOUL by exploiting two different optimization routes. An important advantage of Raman microscopy is that the data can be collected from protein crystals in-situ, in a typical hanging drop plate, under the same conditions used to grow the crystals, thereby ensuring sample stability and allowing its subsequent use in other experiments [1,2].

By extending a recent investigation [3], the present work focuses on some spectral regions, where the vibrational spectra of proteins are sensitive to changes occurring in polypeptide secondary structure and conformation. In particular, it considers the regions of Amide I and Amide III bands, which show quite strong spectral intensity and the wavenumbers of which can be correlated with dihedral angles and hydrogen bonding, thus revealing secondary-structure characteristic features. Moreover, it also deals with some side-chain marker bands, observed in the Raman spectra of SOUL crystals; the unambiguous assignment of these peaks is inferred by comparing the experimental Raman spectra of pure amino acids and their Raman intensities computed using quantum chemical calculations. Our comparative analysis allows to get a deeper understanding of the side-chain environments and of the interactions involving these specific amino acids. These results confirm the potential of Raman microscopy as a reliable and non-invasive tool for novel in-depth structural investigations in biocrystallography.

Keywords: protein crystals, Raman spectroscopy, quantum chemical computation

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III.E. Materials 2

Aurélien Perera, Université Pierre et Marie Curie, France
"The Micro-Structure Of Liquid Water"

Helen Jansson, University of Gothenburg, Sweden
"Slow dynamics in hydrogen bonded liquids"

Mehran Mostafavi, Université Paris-Sud, France
"Solvation Dynamics of Electron in Liquid Polyols, Solvent molecular structure effect"

Huib J. Bakker, FOM Institute AMOLF, The Netherlands
"Water molecules in hydration shells reorient highly anisotropic"

Klaas-Jan Tielrooij, FOM Institute AMOLF, The Netherlands
"Hydrated protons as antennas for vibrational energy"

OP 22: The Micro-Structure Of Liquid Water

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Despite numerous works, the exact microscopic structure of liquid water is still elusive. Is it a network of Hbonds, and if so how to adapt to an associated liquid a concept defined for soft-matter physics? Is it a percolated network? Is it a mixture of two types of liquids, Hbond-ordered and disordered? Each of these model pictures seems only partially adapted to describe this particular liquid. What all these models seem to acknowledge, however, is that liquid water is both a disordered state of matter and ordered locally by the Hbonding interaction, and the right questions to ask seem to be: what is the extension of this local order, and how to unambiguously (model free) prove it?

In this work, we propose to examine the micro-structure of water through the detailed analysis of the most natural probe available in Statistical Mechanics, namely the radial distribution function (RDF). This quantity has been measured by many independent scattering experiments and discussed several times in the literature. It appears, however, that two particular features of this function have been overlooked.

Through the analysis of several popular force field models (SPC/E and TIPnP), we show that [1] the RDF of water possesses a compact structural correlation over three molecular diameters, which is followed by an apparent *extinction* of correlations beyond $R_c \approx 9-10 \text{ \AA}$. This is in stark contrast with the RDF of a typical disordered liquid. This structure is identically reproduced by various models, and tested for different system sizes and simulation conditions and is not an artifact of the simulations of the models. More importantly, it seems to be preserved in aqueous binary mixtures of very different organic solutes, even up to equimolar mixtures in some cases.

By studying the corresponding structure factor[1] and a core-softened model[2] with two length scales, we propose the following picture of the micro-structure of liquid water[1]. The dense packing and the strong Hbond correlations permanently give rise to "excitations" of spatial extension $2R_c$, corresponding to the observed three-peak structure. These excitations weakly interact between themselves, which explains why the spatial correlations beyond are extinct as the cooperative outcome of the competition between the molecular packing and the hydrogen bond induced ordering.

Keywords: Water, micro-structure, radial distribution function.

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OP 23: Slow dynamics in hydrogen bonded liquids

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In addition to the viscosity and glass-transition related main (α) relaxation and the faster and more local secondary (β) relaxation(s) some glass formers, such as e.g. mono-alcohols, are known to exhibit also a slower relaxation process of Debye type. The origin of this slow relaxation is not exactly known, but has been suggested to be due to the relaxation of some kinds of superstructures in which the alcohol molecules, via strong hydrogen bonds, are connected in clusters, chains or micelles [1-3].

Here we will show recent results from mainly dielectric spectroscopy (DS) and differential scanning calorimetry (DSC) measurements that reveal that also other hydrogen bonded liquids, such as polyols and mixtures of polyols and water, display a similar Debye-like slow relaxation. However, in contrast to the strong and clearly observable relaxation in the mono-alcohols, this relaxation process, in polyols, is more tricky to observe since it is usually hidden by a large contribution from conductivity and/or electrode polarization that in general is present at low frequencies in a dielectric measurement. Thus, this type of relaxation process seems to be a more universal feature of hydrogen bonded liquids than previously believed, and, furthermore, it probably has important structural implications.

Keywords: dielectric spectroscopy, relaxations, liquids

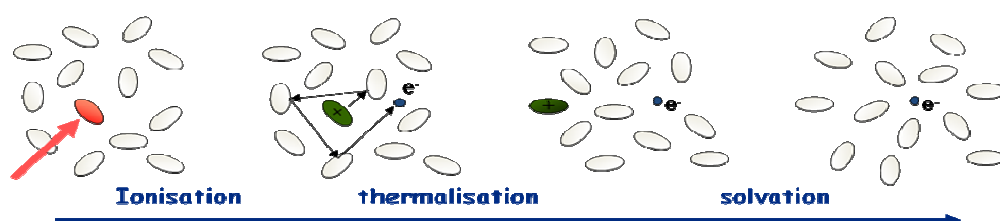
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OP 24: Solvation Dynamics of Electron in Liquid Polyols, Solvent molecular structure effect

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After the first observation of the hydrated electron by microsecond pulse radiolysis experiments in 1962, a main challenge was to resolve its formation dynamics. The limitation of detection time resolution at that moment prevented the study of electron solvation dynamics in water. However, thanks to their low viscosity and low freezing point as well as their wide variety, alcohols became liquids in which solvation dynamics can be studied. The first important results in alcohol were obtained at low temperature using nanosecond pulse radiolysis setup.² It was shown that, early after the pulse, the electron is partially solvated and then its solvation dynamics can be followed by time-resolved absorption spectroscopy. In the 80's, femtosecond pump-probe techniques provided decisive insights in the electron solvation dynamics study in liquids, including water in which it was observed that the electron is fully hydrated in less than a few picoseconds. Since, numerous studies have been conducted in water and methanol, with better time and spectral resolution.



Despite these studies, many important questions remain open: what is the nature of the intermediate species observed before the formation of the fully solvated electron? How the structure of the solvent molecules is involved in the solvation dynamics? Several kinetic mechanisms have been proposed for the solvation processes in water or alcohols. Our group contributed to that discussion by studying the electron solvation dynamics in a previously unstudied series of alcohols: polyols. Polyols have a high viscosity that allows to use a liquid jet sample and to extend the solvation dynamics. In addition, the solvated electron absorption spectrum in these solvent is localized in the visible range. Finally, the use of polyols enables us to investigate the effect of molecular structure of the liquid on the electron solvation dynamics by using several related molecules.

Keywords: Solvation dynamics, electron localization, H-bound effect

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OP 25: Water molecules in hydration shells reorient highly anisotropic

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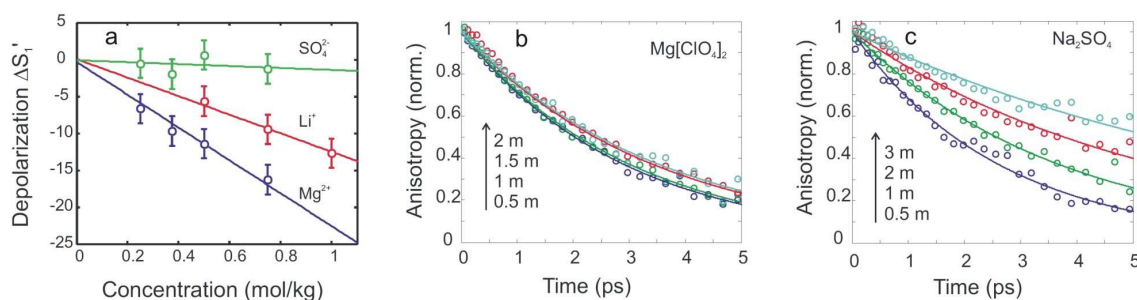
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We study the orientation dynamics of water molecules in the hydration shells of ions and hydrophobic molecules with polarization-resolved femtosecond mid-infrared spectroscopy (fs-IR) and terahertz (THz) time-domain spectroscopy (THz-TDS). The combined application of these techniques to the same solution provides important new insights in the molecular reorientation of solvating water, because the two techniques probe the reorientation of different axes of the water molecule. As a result, existing controversies on the effects of ions and hydrophobes on water dynamics can be resolved.

In the fs-IR experiments, we measure the orientation dynamics of the OD group of HDO molecules dissolved in H₂O, by probing the anisotropy dynamics of the excitation of the OD stretch vibration. In the THz-TDS studies, we determine the orientation dynamics of the permanent dipole moment \mathbf{p} of the water molecule, i.e. the bisector of the water molecule, by probing the polarization response of the solution to a far-infrared electric field.

For solutions containing cations that strongly interact with water, like Mg²⁺, we observe a strong depolarization effect with THz-TDS (Fig. a) and a negligibly small effect with fs-IR (Fig. b). In contrast, for solutions containing anions that strongly interact with water, like SO₄²⁻, we observe little effect with THz-TDS (Fig. a) and a strong slowing down of the reorientation of the hydrating water molecules with fs-IR (Fig. c). These results show that water molecules in the hydration shells of ions are strongly hindered in their orientation mobility, but only in certain directions. For instance, it follows that for a water molecule hydrating a cation, \mathbf{p} is immobilized as this vector is pointing away radial from the cation and, leading to a strong depolarization effect in THz-TDS. However, in this configuration rotation of the OD/OH around \mathbf{p} is still possible, leading to a bulk-like rotation time of 2.5 ps observed with fs-IR. When both strongly interacting cations and anions are present, we observe an interesting cooperative effect that may lead to a new view of the Hoffmeister effect of ions on the structural dynamics of water.

For hydrophobic molecular groups we observe a strong effect with both fs-IR^{1,2} and THz-TDS, showing that for water molecules in the hydrophobic hydration shell the orientation mobility of the permanent dipole \mathbf{p} and the OD/OH groups are both strongly slowed down.



Keywords: water, femtosecond dynamics, hydration shells, ions, hydrophobes

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[2] C. Petersen, K.-J. Tielrooij, and H.J. Bakker, *J. Chem. Phys.* **130**, 214511 (2009).

OP 26: Hydrated protons as antennas for vibrational energy

K-J. Tielrooij, R.L.A. Timmer, H.J. Bakker

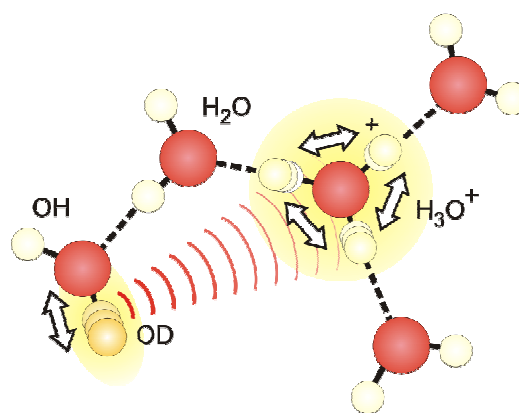
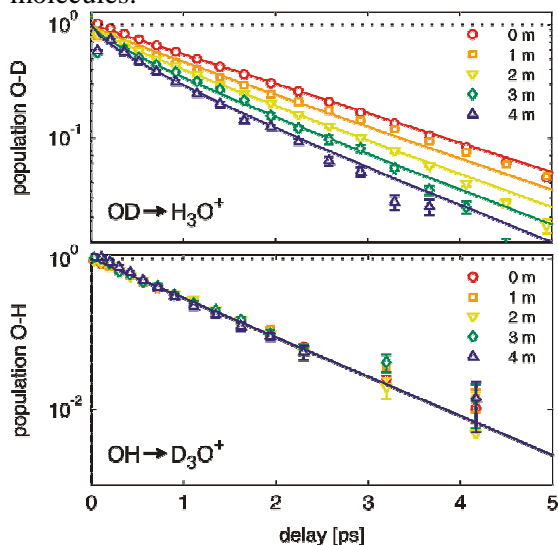
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Protons in water are associated with important processes in nature and technology. Protons in water are not transported by ordinary diffusion, but by a special conduction mechanism that relies on the strong interactions between protons and water molecules.

Here we study the vibrational energy transfer dynamics between water molecules and hydrated protons with femtosecond mid-infrared spectroscopy. We measure the vibrational relaxation of the OD(OH) vibrations of HDO molecules dissolved in H₂O(D₂O), to which we add a mixture of NaClO₄ and HClO₄(DClO₄). We vary the ratio H⁺(D⁺)/Na⁺ keeping the total molality equal to 4 mol/kg. When examining the OD vibration of HDO in H₂O/NaClO₄/HClO₄, we observe that the presence of hydrated protons opens up an additional, non-exponential relaxation channel. Interestingly, for the complementary system of the OH of HDO in D₂O/NaClO₄/DClO₄, the presence of hydrated deuterons has no effect at all on the relaxation dynamics. This finding shows that the acceleration observed for OD is not due to structural changes in the hydrogen-bond network and/or proton transfer events.

The two systems have one major difference: the OD stretch frequency of ~2500 cm⁻¹ overlaps with the broad absorption band of the hydrated proton, while the OH stretch frequency of ~3400 cm⁻¹ does not overlap with the absorption band of the hydrated deuteron. Hence, the additional relaxation channel that opens up for the OD appears to be resonant Förster energy transfer from the OD to the hydrated protons. The energy taken up by the proton vibrations will be quickly dissipated with a T₁ of 110 fs¹. Modeling of the data confirms this picture and shows that the energy transfer takes place over an average distance of ~5 Å, i.e. two water molecules.



We thus demonstrate a new form of coupling between vibrational modes of different character that, in contrast to conventional anharmonic couplings, is highly non-local in character. Hydrated protons are particularly efficient in this non-local interaction because of the large cross-section of their vibrations. As the proton spectrum is extremely broadband, this coupling will occur to all infrared-active molecular vibrations in solution with frequencies <3000 cm⁻¹.

Keywords: water, protons, femtosecond dynamics, energy transfer

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IV Posters

IV.A. Section A

P-A 1: Use of Mass Spectrometry in The Study of Tautomeric Systems in Gas Phase

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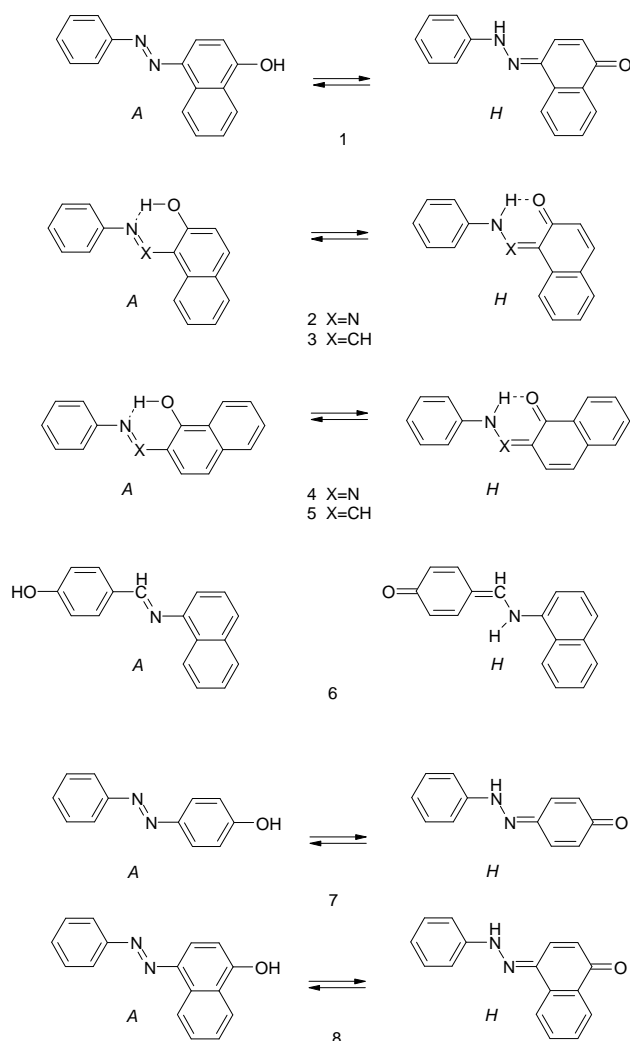
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Tautomerism in organic chemistry has been extensively studied in condensed phase by spectrometric methods, mainly by UV-Vis and NMR techniques. Mass spectrometry (MS) recently has been recognized as a tool for investigation of tautomerism in the gas phase. The use of mass spectrometry is based on the assumption that there is no significant interconversion between the tautomers in gas phase following the electron ionization. Hence, MS provides a snapshot of the tautomeric gas phase mixture and normally the $M^{+\bullet}$ does not undergo tautomerization following evaporation and ionisation in the ion source. As a result, the different pathways of fragmentation of the tautomeric intermediates can be used for identification of the individual tautomers. Consequently, the mass spectrometry can provide valuable information in regard to tautomeric equilibria when studying mass spectra among the members of different families of organic compounds.

Therefore, the aim of this presentation is to show the applicability of GC/MS in the study of tautomeric systems. For this pilot study we have selected number of well known and intensively studied by NMR and UV-Vis spectroscopy tautomeric compounds (The Scheme). Three are the main objectives of the investigation: a) to validate the approach for quantitative analysis in gas phase by using of model compounds (fixed tautomers, where the tautomeric proton is replaced by a methyl group); b) to prove the existence of both tautomers in gas phase and compare the experimental facts about their ratio with the respective UV-Vis spectroscopy observations; c) to investigate the mass spectral behavior as function of the intramolecular hydrogen bonding.

The support by The Bulgarian National Fund (Grant TK01/0478) is gratefully acknowledged.

Keywords: mass spectrometry, proton transfer, hydrogen bonding



P-A 2: Experimental and theoretical study of the $\nu_1(\text{HF})$ band shapes in H-bonded complexes in the gas phase. The $(\text{CH}_3)_2\text{CO}\dots\text{HF}$ complex

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The anharmonic interaction between the high-frequency and low-frequency vibrational degrees of freedom of complexes, in conjunction with the strong vibration–rotation interaction, plays a crucial role in the formation of spectra of hydrogen-bonded systems in the gas phase. The investigation of these interactions is among the topical problems of modern spectroscopy. Special interest represents the study of molecular complexes involving hydrogen halide molecules. The treatment of spectra of these systems is especially fruitful since the spectra possess a rich structure, which allows one to derive many electro-optical parameters from the measured spectra and to assess the validity of the approaches adopted in calculation.

Recently we studied the high resolution spectra of B/HF mixtures, (B = HCN, H₂O and (CH₃)₂O) which were recorded in the gas phase at room temperature [1, 2]. The absorption bands of free molecules and complexes were separated, and the $\nu_1(\text{HF})$ band structure of the B...HF complexes was analyzed in detail. In this study particular attention is paid to the complex (CH₃)₂CO...HF.

Absorption spectra of complexes of hydrogen fluoride with acetone for normal and deuterated monomers were recorded with Bruker IFS-113v and Bruker IFS-125 HR vacuum Fourier spectrometers at a resolution of 0.1 cm⁻¹. The $\nu_1(\text{HF})$ band of the (CH₃)₂CO...HF and (CD₃)₂CO...HF complexes lies in the region of 3900–3200 cm⁻¹ and has a complicated shape with a strongest component at 3450 cm⁻¹.

The spectrum of HF with totally deuterated acetone in the region of the $\nu_1(\text{H-F})$ band was reconstructed nonempirically. The reconstruction is based on an ab initio calculation of the potential energy and dipole moment surfaces at the MP2/6-311++G(2d,2p) level with the BSSE correction taken into account. The electro-optical parameters are obtained from variational solutions of 1D, 2D, and 3D anharmonic vibrational problems. The theoretical value of the $\nu_1(\text{H-F})$ fundamental transition frequency is in good agreement with the experimental data. These solutions provide information about the influence of low-frequency intermolecular modes on the H–F stretch band. The effects associated with the H-bond stretch and rotation of the acetone molecule are most strong. The theoretical spectrum reconstructed as a superposition of rovibrational bands associated with the fundamental, hot, sum, and difference transitions reproduces the shape and separate spectral features of the experimental spectrum. Comparison of the $\nu_1(\text{H-F})$ band shape in the absorption spectra of complexes of HF with water, ether, and acetone shows the dependence of the $\nu_1(\text{H-F})$ band structure on the H-bond strength, the barrier height for tunneling, and rotational constants of subunits. In the complex with acetone, the roles of in-plane and out-of-plane librations of the proton acceptor differ from those in the complexes with dimethyl ether and water because of a different role of the oxygen atom in chemical bonding.

Keywords: absorption spectra of H-bonded complexes in the gas phase, calculation of multidimensional vibrational problem, nonempirical reconstruction of spectra

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Acknowledgment This study was supported by the Russian Foundation for Basic research, Grant 09-03-32272.

P-A 3: Hydrogen bond network topology in aqueous solutions

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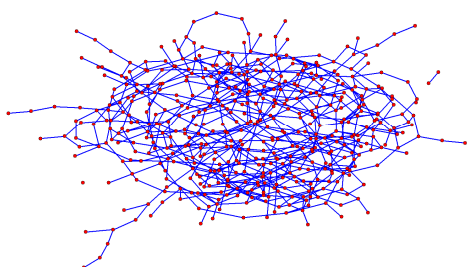
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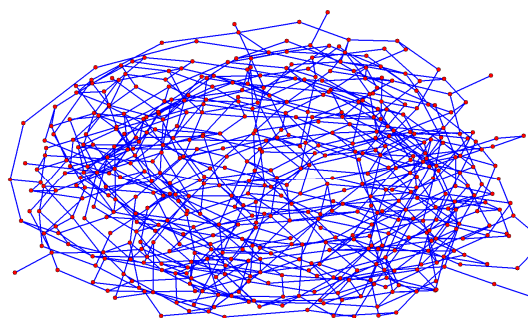
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. Series of A molecular dynamics simulation has been performed to study the structure of water-methanol and water-formamide mixtures. Besides the evaluation of partial radial distribution functions describing the hydrogen-bonded structure of the mixtures with different composition, the clustering properties and topology of hydrogen-bonded network were investigated as well. The results have shown that mixtures of methanol and water and of formamide and water exhibit an extended structures in solution. At low methanol concentration water molecules form a percolated network, methanol molecules are incorporated as monomers or short chains and together form a percolated system. In methanol-rich mixtures short water- chains and longer methanol chains build up the hydrogen-bonded clusters in the system. On the basis of the statistical analysis of configurations obtained from molecular dynamics simulation it has been found that more methanol molecules are connected to non-cyclic entities, while more water molecules form rings that might have been predicted on the basis of the stoichiometry of the mixtures. This finding can be explained by the presence of microscopic configurational inhomogeneity in water-methanol mixtures. In water-formamide mixtures the molecules form a percolated network. On the basis of same analyses, what we performed on water-methanol mixtures we conclude, that the composition of cyclic entities in these system are very close to the ideal, thus so we find a microscopic homogeneity in this system. The hydrogen bond network topology in water and formamide are shown on Figure.

Formamide



Water



Keywords: simulation, network topology, microheterogeneity, microhomogeneity

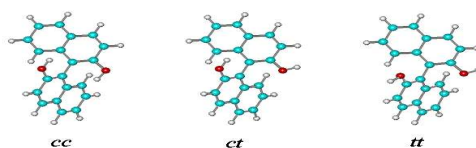
P-A 4: Intramolecular Hydrogen Bonds to π -Acceptors within the Polarizable Continuum Model

Goran Baranović* and Nikola Biliškov

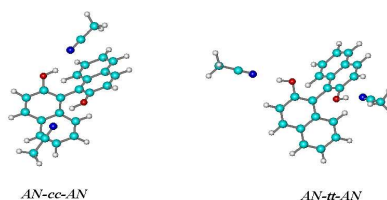
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Intramolecular hydrogen (H) bonds are important because they can stabilize one of the possible (rotational) isomers. The strength of such a bonding, particularly to π -acceptors, is much influenced by the molecular environment and the isomer preference relative to the gas phase can be reversed. The solvent influence on solute isomer equilibrium can be treated within the polarizable continuum model (PCM) by using density functional theory. In this study the measured IR spectra of 1,1'-bi-2-naphthol and 2-ethynylphenol in a series of carefully chosen solvents are used to examine the performances of the used theoretical approach.



The isomers of 1,1'-bi-2-naphthol and 2-ethynylphenol are differing in the positions of their hydroxyl groups. The height of the potential barriers between them was also calculated and the corresponding transition states characterized. In H-bond non-accepting solvents the isomer preference does not change relative to the gas phase although the less stable isomers are more probable in solvents of higher relative permittivity. In H-bond forming solvents the least stable isomer is most probably prevalent due to the additional stabilization through intermolecular H-bonds with solvent molecules. A detailed vibrational analysis revealed the spectral regions specific to the OH vibrations with the observed solvent effects concerning the redistribution of vibrational intensities rather than the wave number shifts.



The question remains about the nature of the solute-solvent complex. For example, in acetonitrile (AN) both types of complexes, AN $\cdots cc \cdots$ AN and AN $\cdots tt \cdots$ AN, are possible. This is applicable also for 2-ethynylphenol. The equilibrium depends on the relative sizes of the various contributions to the enthalpy of complex formation.¹ The latter type seems significantly more probable as shown by calculations and by comparison with similar systems (e.g. phenol and 2-naphthol experimental data) having OH groups attached to an aromatic group but lacking intramolecular H-bond.

Keywords: intramolecular hydrogen bond, π -acceptor, polarizable continuum

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P-A 5: Hydrogen bonds in DABCO mono-betaine studied by X-Ray, FTIR spectra and DFT calculations

Piotr Barczyński, Zofia Dega-Szafran, Andrzej Katrusiak, Waldemar Perdoch, Mirosław Szafran

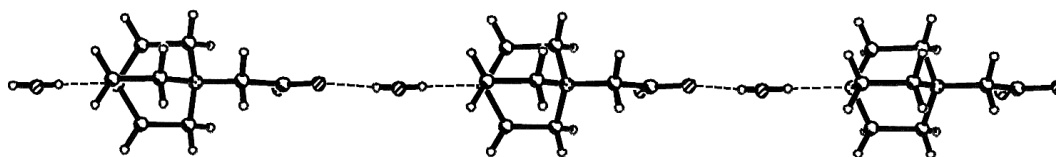
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1,4-Diazabicyclo[2.2.2]octane (triethylenediamine, N(CH₂CH₂)₃N), abbreviated as DABCO, is a globular molecule of high symmetry. It crystallizes in a hexagonal space group P6₃/m [1]. The crystal undergoes a structural phase transition to a plastic phase at 351 K and it melts at 433 K [2,3]. DABCO is a strong base, its pK_a = 8.84 and PA = 230.2 kcal/mol [4].

The aim of this work is the synthesis of 1-carboxymethyl-1,4-diazabicyclo[2.2.2]octane inner salt (DABCO mono-betaine) and its characterization by the spectroscopic methods, X-ray diffraction and DFT calculations.



DABCO mono-betaine crystallizes as monohydrate in orthorhombic space group *Pmn*2₁. The molecules are located on a mirror plane. The water molecules link DABCO mono-betaine into linear chains through the H-O-H...OOC and H-O-H...N hydrogen bonds of 2.709(2) and 2.875(2) Å, respectively.



The structures of anhydrous DABCO mono-betaine and its hydrates are optimized at the B3LYP/6-31G(d,p) level of theory and compared with the X-ray results. The absorption bands in the FTIR spectrum are assigned on the basis of the DFT calculations. The calculated magnetic shielding tensors confirm the assignments of the ¹³C NMR resonance signals.

Keywords: 1,4-diazabicyclo[2.2.2]octane, betaine, X-ray, spectroscopic methods, DFT calculations

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P-A 6: Temperature Dependence of H/D Isotope Effect on NMR Chemical Shift of ^{19}F Nucleus of $[\text{FHF}]^-$ in a Polar Solvent

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^{19}F NMR spectra of partially deuterated in mobile site tetrabutylammonium hydrogen difluoride ($[\text{FHF}]^-$) dissolved in a low-freezing solvent, namely, $\text{CDF}_3/\text{CDF}_2\text{Cl}$, in the temperature range, 110 – 210 K, are recorded and interpreted. A DNMR procedure based on density matrix evolution, using one well-resolved spectrum in the slow exchange regime as zero approximation provided the evaluation of H/D isotope effect on ^{19}F chemical shift within the accuracy $\sim 5\%$ over the whole temperature range. The temperature elevating results in a strong rise of the absolute value of the negative isotope effect on the ^{19}F chemical shift, from -0.3 up to -0.6 ppm in the above temperature range.

Interpretation of the observed temperature dependence was performed in two ways. The first approach implicated only the intermolecular effect, namely, thermal population of excited vibrational states. The surfaces of potential energy and fluorine shielding in normal coordinates were calculated at the MP2/6-311++G** level. The four-dimensional anharmonic problem was solved using a linear variational procedure. The population of 342 excited levels was accounted. The conclusion is that the intrinsic effect of vibrational excitation alone cannot be responsible for the observed, very strong, temperature dependence of the isotope effect.

In the second approach, the alteration of the equilibrium geometry of the ion, caused by changing solvent polarity with temperature rising [1] was implicated using SCRF formalism at the HF/6-311++G** level. Unfortunately, the intermolecular treatment could not be performed at as high level as the intramolecular one. Namely, three one-dimensional anharmonic problems (in normal coordinates) were solved using PT, with the intermode coupling neglected, and the population of only three first excited vibrational states accounted. Such approach has resulted in a qualitative, though far from quantitative, agreement with experiment. In this treatment, the main reason of strong temperature dependence of the NMR isotope effect is stretching the ion with decreasing solvent polarity, due to a strengthening of the electrostatic repulsion of two F^- ions involved. This results in a considerable diminishing of the frequencies of two proton vibrations and, therefore, in the corresponding rise of their amplitudes. The population of the degenerate transversal proton vibration, ν_2 , takes also a perceptible part in the total temperature effect. It should, however, be noted, that the result depends very strongly on the level of solving the electronic problem, so that this conclusion cannot be taken as fully reliable.

The work was supported by RFBR (N 08-03-00615) and NNIO (09-03-91336) grants

Keywords: NMR, Hydrogen Difluoride ion, Temperature Dependence, H/D Isotope Effects

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P-A 7: Anharmonic effects in infrared spectra of hydrogen difluoride ion [FHF]⁻

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There are many papers both experimental and theoretical (see [1]) devoted to the investigation of hydrogen difluoride ion [FHF]⁻. The main attention is paid for the properties of hydrogen bonding probed by using IR and NMR experimental data. However despite of the simplicity of this molecule and the variety of the theoretical approaches applied to the explanation of the IR spectra features there are still remain the challenging problems of reproducing the frequencies and the intensities of the fundamental, combination and overtone bands.

The main goal is to design semiempirical models of potential and dipole moment function which would describe the spectra in the area of interest. Potential energy surfaces (PES) and dipole moment functions (DMS) are computed using the Gaussian'03 package on MP2/6-311++G(d,p) and CCSD/6-311++G(3df,3pd) level calculation. To achieve this aim two approaches are used.

First one is based on the perturbation theory of 2nd order and analytical calculations that give the mechanical and electrooptical anharmonic parameters of both molecules [FHF]⁻ and [FDF]⁻. It allows determining which coordinate basis set (normal or internal) fits best and which model parameters are crucial for reproducing IR spectra. To explore the role of the anharmonic intramode coupling all sorts of anharmonic vibration problems (1D – 4D) were solved.

Second one is the linear variation method. In the framework of the numerical calculation the PES/DMS are stood for the set of single points. To overcome the difficulties of dealing with analytical approximations and to control the accuracy level of the matrix elements the Gauss-Hermit quadratures are used. This computing method allows obtaining the best algebraic degree of accuracy.

The work was supported by RFBR (N 08-03-00615) grant.

Keywords: IR, Hydrogen bond, Hydrogen Difluoride ion, Anharmonicity

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P-A 8: Retention of Hydrogen-Bond Motif in Solid H_2CO_3 : Crystallization of Two Polymorphs from Two Amorphous Forms

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Sarah L. Price³, Erwin Mayer²

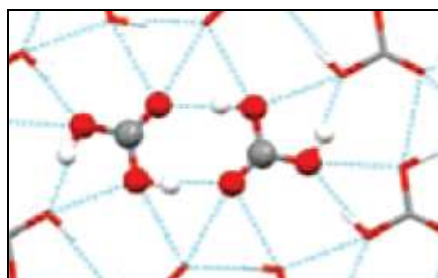
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Since H_2O and CO_2 coexist in various astrophysical environments such as in icy grain mantles in the interstellar medium, the formation of solid or gaseous carbonic acid by high-energy irradiation and its astrophysical significance is being discussed, in particular also on comets such as Halley or on the polar regions of Mars [1]. In the lab solid H_2CO_3 can be produced by (i) high-energy irradiation of cryogenic $\text{CO}_2/\text{H}_2\text{O}$ mixtures [2], (ii) proton irradiation of pure solid CO_2 [3], and (iii) protonation of bicarbonate or carbonate in a new cryogenic technique developed by our group [4]. Depending on whether KHCO_3 and HCl had been dissolved in methanol or in water, revealed formation of two distinct states of amorphous carbonic acid (H_2CO_3), and of their phase transition to either crystalline α - or β - H_2CO_3 [1, 4].



The main spectral features in the IR spectra of α - and β - H_2CO_3 are observable already in those of the two amorphous H_2CO_3 forms. This indicates that H- bond connectivity and/or conformational state in the two crystalline phases is on the whole already developed in the two amorphous forms. The variety of structural motifs found within a few kJ/mol in a computational polymorph search provides a plausible rationalisation for a) the observation of more than one amorphous form and b) the retention of the motif observed in the amorphous form in the corresponding crystalline form. The poly- amorphism inferred for carbonic acid from our FTIR spectroscopic studies is special since two different crystalline states are linked to two distinct amorphous states. We surmise that the two amorphous states of H_2CO_3 are connected by a first- order like phase transition, and report how the Infrared-spectrum [5] and the Raman-spectrum [6] develop from amorphous to crystalline carbonic acid upon heating to ~ 220 K.

Keywords: carboxylic acid, Raman and IR spectroscopy, solid-state structures

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P-A 9: Hydrogen-bonded networks in supercritical and supercooled water

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Liquid state is characterized by the presence of an infinite physical cluster of molecules. The line of the percolation transitions of physical clusters, which marks the first appearance of the infinite cluster, starts from the critical point and extends towards higher temperatures and densities [1]. For water, the hydrogen-bonded cluster is a good approximation of physical cluster. By performing the percolation analysis, we have estimated the location of the line of the percolation transitions of model bulk water with respect to the liquid-vapor critical point [2,3]. The universal values of the probability, that the largest fluid cluster crosses the simulation box in 1, 2 or 3 dimensions at the percolation threshold (crossing probabilities), are 0.79, 0.93 and 0.99, respectively [4]. The high values of the crossing probabilities indicate the existence of rarefied networks spanning over mesoscopic length scales. Such networks should affect various properties of supercritical water, since in a wide range of water density below the percolation threshold they extend over several nanometers.

Water undergoes multiple liquid-liquid phase transitions in supercooled region [5]. In order to clarify the origin of these transitions, we have studied the percolation transitions of water molecules exhibiting the same kind of local ordering [6]. In low-density water, there is an infinite hydrogen-bonded network of the four-coordinated water molecules with the tetrahedral arrangement of the nearest neighbors. Upon increasing pressure, this network breaks and low-density water undergoes transition to normal water. The existence of an infinite network of the tetrahedrally ordered water molecules with any number of the nearest neighbors is characteristic of normal water. Upon further increasing of pressure, this network breaks and the absence of an infinite network of tetrahedrally ordered water molecules is characteristic of high-density water. The transitions of normal liquid water to low-density, strongly tetrahedral water upon cooling and to high-density, weakly tetrahedral water upon pressurization may be responsible for the experimentally observed qualitative changes of the dynamics of hydrated biomolecules [7,8].

Keywords: supercritical water, supercooled water, percolation transition

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P-A 10: Hydrogen bonding and proton transfer in cyclic complexes of bifunctional azo-compounds in solution

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The formation of cyclic complexes under the self-association of bifunctional azo-compounds 3,5-dimethylpyrozole (I), diphenyltriazene (II), diphenylformamidine (III) and their interaction with carboxylic acids was studied by IR absorption spectra in solution and by quantum-chemical calculations. These molecules, which have the basic N atom acting as strong proton acceptor and contain simultaneously proton donor group NH, are favourable to the formation of various H-bonded complexes in gas phase, solids and solutions – cyclic dimers, trimers and tetramers, linear chains and helices, depending on the structure and specific peculiarities of molecule-partner. The IR spectra of solutions in CH₂Cl₂ and CCl₄ show the existence of equilibrium between monomers and cyclic self-associates of the molecules studied, with the formation of cyclic trimers in case of I and cyclic dimers for II and III. The B3LYP/6-31** calculations give the value 179.3° for the NHN angle in trimer structure of I in comparison with 143.6° for dimer; calculated NHN angle in dimer of III is equal to 177° [1].

Under the interaction with weak carboxylic acids (HCOOH, CH₃COOH, CH₂ClCOOH), which are well-known bifunctional oxygen-containing compounds, the complexes have molecular composition with two H-bonds NH...O=C and OH...N in cyclic structure. The proton transfer and formation of cyclic H-bonded ionic pairs were found spectroscopically for the complexes with stronger (CF₃COOH, CCl₃COOH, CHCl₂COOH) carboxylic acids. The interaction with strong acids results in the proton transfer from hydroxyl group of acid to the N atom of the base [2]. It was shown that the IR spectra of the I + trichloro- or trifluoroacetic acid systems revealed drastic changes upon addition of an excess of the acid. In accordance with results of *ab initio* calculations the conclusion was made that these complexes had 1:2 structure and contain homoconjugated ions with strong almost symmetrical H-bonds [3].

The quantum chemical DFT calculations in harmonic and anharmonic approximations confirm the formation of cyclic complexes, while the proton transfer along the OH...N bridge was supported for the complexes with strongest acids. Inclusion of polarizing environment in the framework of Onsager or Tomasi models changes relative depth of minima on the potential energy surface of corresponding system in favour of the ionic form minimum. The geometrical and spectroscopic characteristics were obtained for all systems studied, such as the theoretical simulation of their IR spectra.

To minimize the usual significant difference between results of quantum chemical calculations in harmonic approximation and the experimental data, we attempted calculations of vibrational frequencies and band intensities for molecules studied and their cyclic complexes with acids including the influence of the anharmonic effects. Three different approaches were used. It was shown that the use of variational multidimensional anharmonic approach is the most preferable for calculations of the high-frequency XH stretch in systems where the corresponding normal mode is less characteristic and involves motions of many atoms.

Keywords: solutions, hydrogen-bonded complexes, IR absorption spectra, proton transfer, quantum chemical calculations.

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P-A 11: Infrared study of the structure and dynamics of internally hydrogen bonded molecules isolated in parahydrogen matrices

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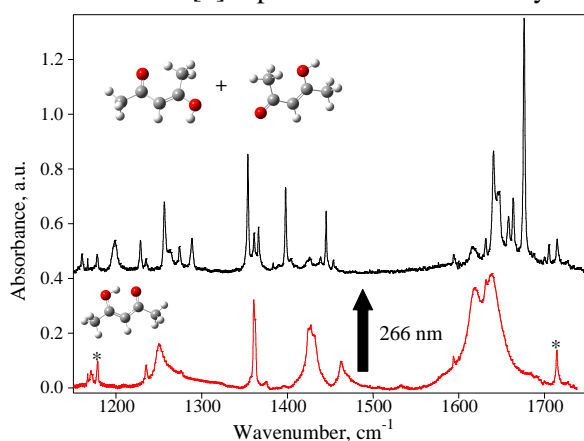
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Molecules with internal hydrogen bond are attracting scientific attention from the beginning of the 20th century. Despite numerous theoretical and experimental studies, a number of structure and dynamic aspects, even for the smallest molecules such as Glycolaldehyde (GA) or Acetylacetone (AcAc), remains under question [1-3].

Infrared spectroscopy combined with matrix isolation technique provides a powerful tool to study various properties of molecular systems. Solid molecular hydrogen crystals with all molecules in the $J=0$ rotational state is recently widely recognized as a very attractive media for the matrix isolation experiments [4]. Hydrogen molecule in the $J=0$ state has anti-parallel nuclear spins resulting in absence of dipole quadruple or higher moments. Very weak interaction and "softness" of molecular hydrogen crystal results in a very small perturbation on the molecules isolated in such environment. These properties of the matrix allow to obtain very sharp spectral bands of the molecule under study.

Our studies of infrared spectra of GA and AcAc isolated in pH_2 show similar patterns as those isolated in other matrices [2]. Spectral bands are usually sharper in pH_2 than in other matrices. Very important feature of



Infrared spectra of acetylacetone isolated in pH_2 matrix at 4 K before (bottom) and after (top) UV irradiation
Asterisk denotes keto tautomer bands

pH_2 is that no notable matrix split was observed. This facilitates more accurate assignment of the spectral bands which is important for the studies of conformational diversity, isomerization processes and possible hydrogen bond complexes. Experiments with added water allow us to observe and assign spectral bands of water-Ga complex.

Infrared studies of AcAc revealed that the most stable structure in matrices is enolic, C_s symmetry planar ring, in contrary to C_{2v} recently proposed in the gas phase [3]. About 7 % of keto tautomer of AcAc was observed in the pH_2 matrices; "keto" bands are thus assigned for the first time. Photoisomerization experiments using quadruple YAG radiation revealed four additional stable forms of AcAc which is in perfect agreement with works performed by S. Coussan et al. [1]. These new

experiments allow an improvement of vibrational assignments of various isomers.

Keywords: Matrix isolation, parahydrogen, internal hydrogen bond

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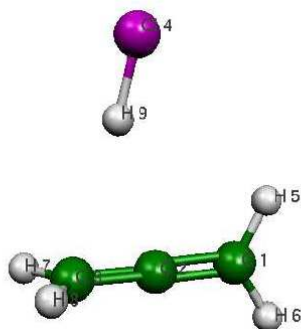
**P-A 12: High resolution infrared spectroscopy of molecular complexes M-HCl.
From experimental data to intermolecular potential.**

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We have observed for the first time the C₃H₄-HCl complex in gas phase. A previous IR observation in cryogenic liquid existed but without rotational resolution [1]. Two new IR spectra have been recorded, the first one in a cooled cell, the second one at higher resolution in a molecular jet. Rotational constants and vibrational frequencies have been obtained from these spectra. These experimental data are presented and compared with the high level ab initio calculations (CCSD(T)/cc-pvtz) that we have done in collaboration with the group of V. Brenner (CEA Saclay, France). Then the series of these small systems formed by complexation of hydrogen chloride with acetylene, ethene [2-4] and this new one is presented.



Mainly, the results show an evolution of the predissociation time with the size of the system and also a variation of the vibrational shifts correlated to the proton affinity of the base M.

Keywords: IR spectroscopy, high resolution, hydrogen bonded complexes.

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P-A 13: Hydrogen bonds in complex of quinuclidine betaine with tartaric acid

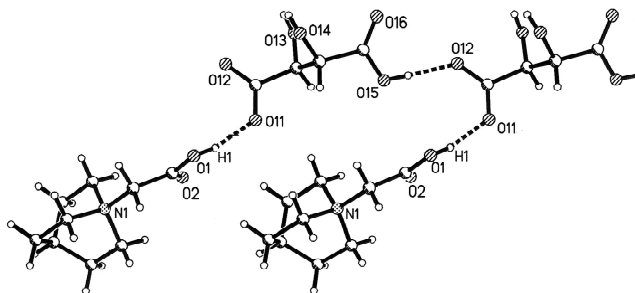
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Quinuclidine (1-azabicyclo[2.2.2]octane) is a strong base ($pK_a = 11.15$) and has poorer steric requirements compared to triethylamine [1]. Recently, we studied the structure of quinuclidine betaine hydrate (N-carboxymethyl-quinuclidinium inner salt, QNB-H₂O) [2]. In this paper we describe the structure of the complex of quinuclidine betaine with L(+)-tartaric acid (TA). Salts of tartaric acid with amines show either 1:1 or 1:2 stoichiometry. Several hydrogen-bonded L(+)-tartaric-amine salts exhibit a second harmonic generation (SHG) properties [3-5].

The complex of quinuclidine betaine (QNB) with L(+)-tartaric acid (TA) is of 1:1 stoichiometry. It crystallizes in monoclinic space group $P2_1$. In the crystal quinuclidine betaine is protonated and interacts with semi-tartrate anion by the short O(1)-H...O(11) hydrogen bond of 2.472(4) Å. The semi-tartrate anions form infinite chains through the hydrogen bonds formed between the carboxylic and carboxylate groups of the neighbouring TA molecules, with the O(15)-H...O(12) distance of 2.585(5) Å.



The FTIR spectrum shows two broad bands in the 2700-2200 and 2000-500 cm⁻¹ regions typical of medium and short hydrogen bonds, respectively. In the optimized structures of the title complex at the B3LYP/6-31G(d,p) level of theory both in the monomer, QNB-TA, and dimer, (QNB-TA)₂, the betaine molecules are not protonated. The ¹H and ¹³C NMR spectra elucidate the structure of the complex investigated in aqueous solutions.

Keywords: 1-azabicyclo[2.2.2]octane, betaine, O-H...O and O-H...N hydrogen bonds, DFT calculations

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P-A 14: Sevoflurane, a study of a complex situation

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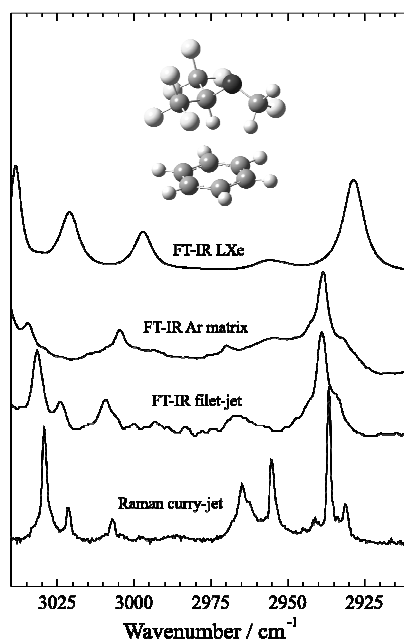
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Sevoflurane is one of the prevalent anesthetics. Millions of patients every year put their trust in this drug, even though, molecular interaction mechanisms are poorly understood. Recent work has shown that anesthetics interact directly with specific proteins through unique binding sites, where aromatic rings serve as main targets [1]. In this study the formation of a C-H \cdots π bonded complex between sevoflurane (CF₃)₂CHOCH₂F and the simplest aromatic ring, benzene, has been examined using jet, matrix-isolation and cryosolutions infrared- and Raman spectroscopy.

Analysis of the cryosolutions and supersonic jet spectra of low sevoflurane concentrations vs. the supersonic jet spectra of high concentrations and those obtained with matrix-isolation, led to the assignment of the fundamental vibrations of sevoflurane. In particular the assignments in the C-H stretching region allow the identification of the stretching mode of the C-H bond involved in the formation of the complex. That mode was observed in the complex to red-shift by 4.2(1) cm⁻¹. The standard complexation enthalpy of the 1:1 complex was measured to be -10.0(2) kJ mol⁻¹. The experimental results have been compared with ab initio calculations at the MP2/(aug)-cc-pvdz level. The complexation enthalpy characterizes the interaction as a weak hydrogen bond, similar to those found in the complexes of other anesthetics [2,3].



Keywords: sevoflurane, C-H \cdots π hydrogen bond, FTIR, Raman, cryosolution, supersonic jet, matrix

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P-A 15: Comparative studies of intramolecular proton transfer and charge delocalization in Schiff bases derivatives of orto-hydroxynaphthaldehydes

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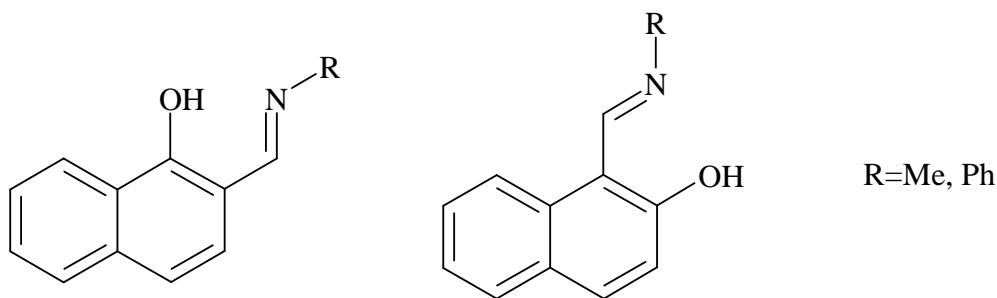
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Important biological and physico-chemical properties as well as possible practical application of the Schiff bases, derivatives of aromatic orto-hydroxyaldehydes are directly related to the presence of the intramolecular bond and proton transfer equilibrium.

Proton transfer equilibrium for N-(1-hydroxy-2-naphthylidene)-methylamine in CDCl₃ and DMSO-d₆ have been established by means of NMR spectroscopy and compared with the respective values for its isomer N-(2-hydroxy-1-naphthylidene)-methylamine [1] and their analogues derivatives of aniline [2].



Influence of the structural and solvent effects on the position of the proton transfer equilibrium in the Schiff bases derivatives of o-hydroxynaphthaldehyde have been shown. Interralation between the intramolecular hydrogen bond and π -electron delocalisation have been discussed based on the calculated HOMA parameters.

Keywords: Schiff bases, intramolecular hydrogen bond

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P-A 16: Weakly bound electrons in large sodium doped water clusters

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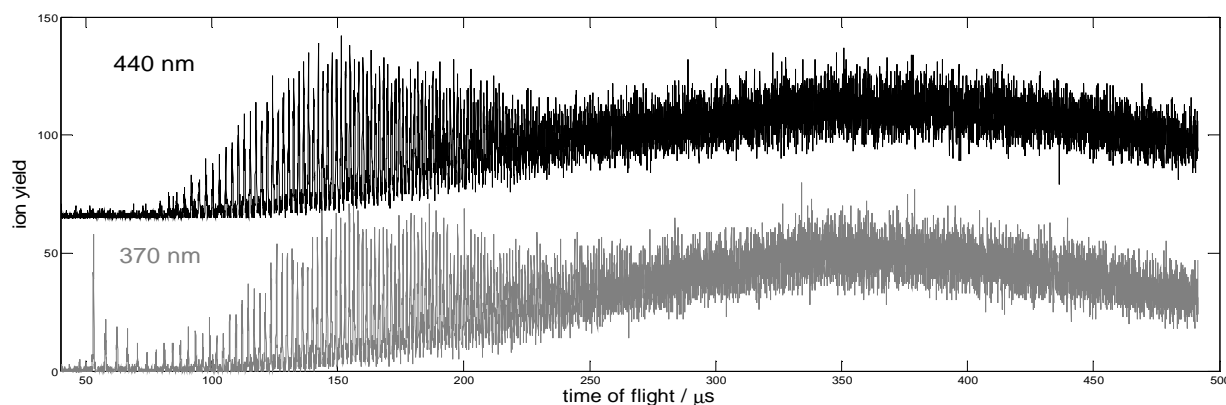
For $M(\text{H}_2\text{O})_n$ $M=\text{Na}$ [1, 2], Cs [3], Li [4] clusters constant ionization potentials (IP) of about 3.2 eV for $n>5$ are found. This value is also valid for other OH bonded solvents like methanol [5] and ethanol. Although in theoretical studies different binding motifs are classified [5,6,7], no experimental discrimination of binding states by ion yield evolutions with photon energy has been reported yet.

In contrast to the IPs, for the vertical binding energy (VBE) for $(\text{H}_2\text{O})_n^-$ and $(\text{MeOH})_n^-$ three respectively two different isomers are found [8,9].

In our experiment we investigated water clusters in a size range of $n=3, \dots, 450$ which are generated in a supersonic expansion and doped with sodium atoms using a pick-up-cell. Subsequently the clusters are photoionized by tuneable laser light with $\lambda=360$ nm to $\lambda=460$ nm in 5 nm steps and size selected with a reflectron time-of-flight mass spectrometer.

In Figure 1 the ion yield of $\text{Na}(\text{H}_2\text{O})_n$ clusters is compared for 370 nm (3.35 eV) and 440 nm (2.82 eV). The size distribution is similar, except for the range of small clusters with $n \lesssim 12$, where no cluster abundance is seen at 440 nm.

Figure 1:



This indicates the existence of a weakly bound electron in large sodium doped water clusters ($n>12$) with an IP of ≈ 2.8 eV.

Keywords: Microsolvation, Water Clusters, Ionization Potential

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P-A 17: Theoretical Studies of Hydrogen Bonded Complexes of Methanol and Dimethylamine with Some Common Electron Donors

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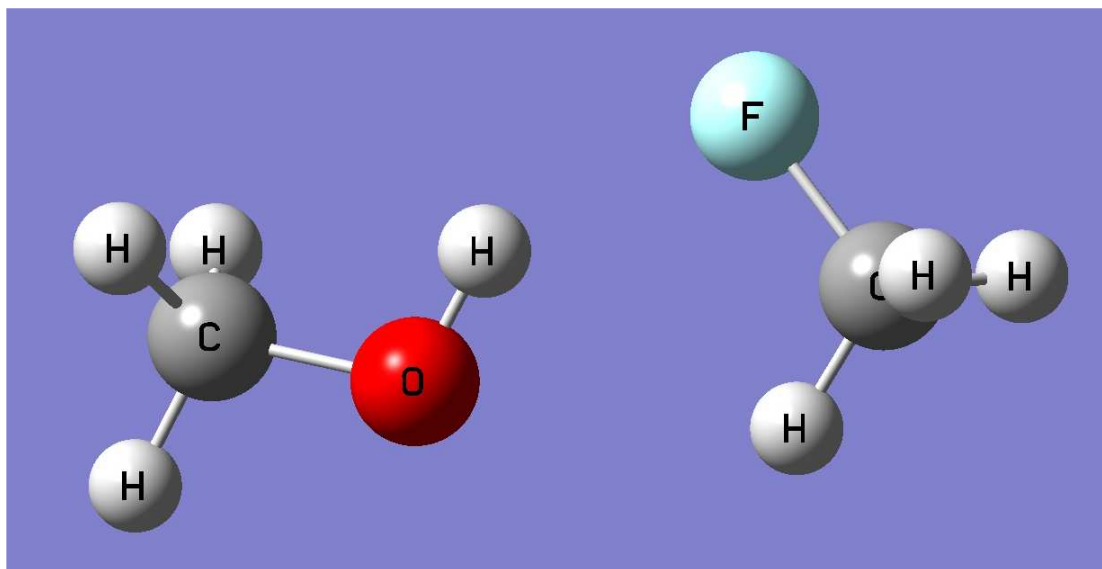
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ABSTRACT

The properties of the hydrogen-bonded complexes of methanol and dimethylamine with a series of electron donors have been studied by means of a series of *ab initio* molecular orbital calculations. The bases selected were the fully-methylated derivatives of ammonia, water, phosphine and hydrogen sulphide, in addition to methyl fluoride and methyl chloride. In this way the tendencies of the common proton donors methanol and dimethylamine to form hydrogen-bonded complexes with nitrogen, oxygen, fluorine, phosphorus, sulphur and chlorine bases, in which the substituents are exclusively methyl groups, have been determined and compared. The properties studied are the interaction energies, the O(N)...X separation distances, the enhancements of the OH(NH) bond lengths, the OH...X(NH...X) bond angles, the OH(NH) stretching wavenumber shifts and the increases of the infrared intensity of the OH(NH) stretching vibrations (X = N, O, F, P, S, Cl). These properties are rationalized on the basis of the natures of the interacting partners.

Keywords: methanol, dimethylamine, structures, hydrogen bond energies, vibrational spectra.



P-A 18: The pK_a Slide Rule as a Tool for Predicting Hydrogen-Bond Strengths

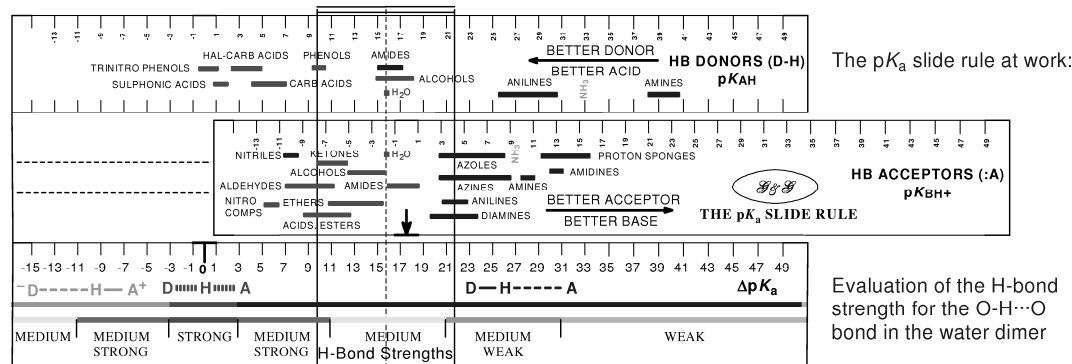
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D–H...:A H-bonded interactions (D and :A = H-bond donor and acceptor) display a wide interval of binding energies, E_{HB} , ranging from less than one to more than 30 kcal mol⁻¹ (45 kcal mol⁻¹ if [F...H...F]⁻ bonds are considered) because of two independent factors: (i) H-bonds are the stronger the more electronegative the donor (D) and acceptor (:A) atoms are [1,2]; (ii) for a same D–A couple [or *H-bond electronegativity class*, $EC(D,A)$] H-bonds are the stronger the more similar the proton affinities of D and A are, a fact easily expressible in terms of the *PA/pK_a equalization principle* [3-5] for which really strong H-bonds can be observed only when the differences $\Delta PA = PA(D^-) - PA(:A)$ or $\Delta pK_a = pK_a(D-H) - pK_a(A-H^+)$ tend to zero (PA being the gas-phase proton affinity and pK_a the co-logarithm of the corresponding acid-base dissociation constant in water). These properties are at variance with all other types of chemical bond and derive from the *dual nature of the H-bond*, which is not really 'a bond' but rather 'two bonds' formed by a same central proton with the two lone pairs located on the so-called donor and acceptor atoms.

These considerations emphasize the role played by *PA/pK_a equalization* in strengthening the H-bond, a hypothesis often invoked but never fully verified in the past which is now reconsidered in this communication by a new instrument, *the pK_a slide rule*. This is a bar-chart reporting, in separate scales, the pK_a 's of the D–H proton donors and :A proton acceptors most frequently involved in D–H...:A bond formation (103 entries over the $-14 \leq pK_a \leq 53$ range). Allowing the two scales to shift so to bring into coincidence the donor and acceptor molecules, the ruler permits graphical evaluation of ΔpK_a and then empirical appreciation of D–H...:A bond strengths according to the pK_a equalization principle.



Keywords: PA/ pK_a equalization principle, pK_a slide rule, H-bond strength prediction

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P-A 19: NMR Study of Hydrogen Bonds Geometries in Homo- and Hetero-Conjugates of Carboxylic Acids

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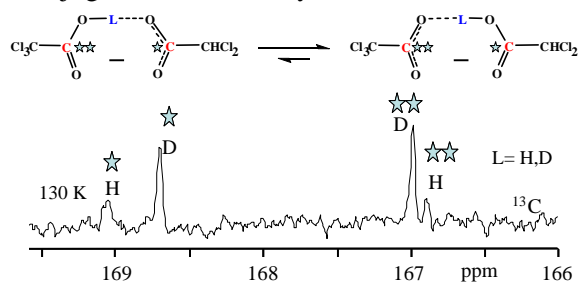
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In this work we present our study of hydrogen bond geometries of homo- and heteroconjugated anions of acetic, chloro-, dichloro-, trichloro- and trifluoroacetic acids with tetraethylammonium as counter ion. This series of complexes gives the set of "snapshots" of the proton transfer pathway. The compounds were dissolved in CDF₃/CDF₂Cl and studied by ¹H, ²H and ¹³C NMR spectroscopy at temperatures down to 120 K.

We first considered medium-strong H-bonds in hetero-conjugate in which only one tautomer exists. In this case $\delta^1\text{H}$ can be directly converted into the hydrogen bond geometry using previously established correlations.^[1,2] We show that the IE on $\delta^{13}\text{C}$ in COOH...O- and COO...HO bonds have opposite signs, with which one can determine on which side of the H-bond center the bridging proton is located. Then we have examined a series of homoconjugated anions for which $\delta^1\text{H}$ (19-21 ppm) are not affected by degenerate proton tautomerism and can be converted into a pair of intrinsic H-bond geometries. In contrast to $\delta^1\text{H}$, the isotope effects on $\delta^{13}\text{C}$ are 50/50 averaged between two intrinsic values. The overall dependence of IE on $\delta^{13}\text{C}$ on proton position is dispersion-like, similar to that in case of ¹⁵N^[3] and ¹⁹F^[4].

We also studied a series of hetero-conjugates, which are subject to asymmetric proton tautomerism and thus only qualitative conclusions can be made. For example, we show that the same sign of the IE on $\delta^{13}\text{C}$ for both carboxylic carbon atoms in R₁COOH...OOCR₂ complex is an indication of a significant contribution of the proton tautomerism.



Keywords: hydrogen bond geometry, H/D isotope effect, proton tautomerism

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P-A 20: ^1H and ^{15}N NMR Study of Hydrogen Bonding of the Amide Group in Heterocyclic Amides

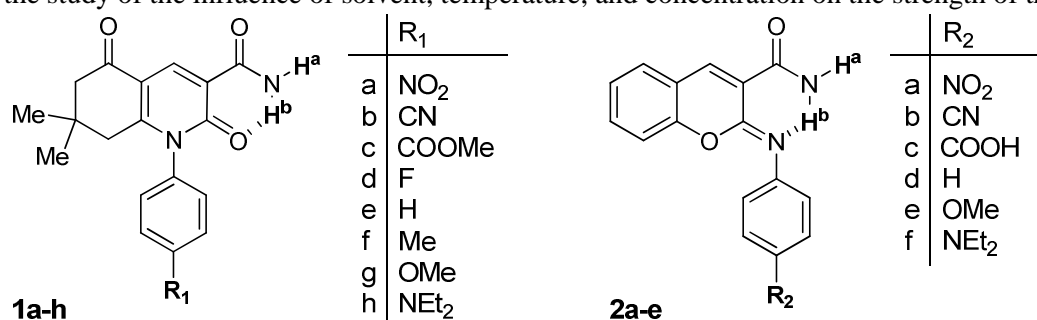
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The important role of hydrogen bonded amides in stabilization of space structure of proteins and other biopolymers as well as in self-assembling nanocomplexes is of particular interest to scientists studying small model molecules which contain intra- or intermolecular hydrogen bond (H-bond) of amide group. In these model compounds the chemical shifts of the amide hydrogen bonded proton can be used as a spectral index for the study of the influence of solvent, temperature, and concentration on the strength of the H-bond.



Herein we present our comparative study of 1,2,5,6,7,8-hexahydro-7,7-dimethyl-2,5-dioxo-1-arylquinoline-3-carboxamides (pyridones) **1a-h** and 2-aryliminocoumarin-3-carboxamides **2a-f** containing intramolecular H-bond of the amide group. The model molecules are heterocyclic primary amides with one of the amide protons involved in intramolecular hydrogen bonding with proton-acceptor group. In the case of the pyridones **1** the proton-acceptor C=O group is affected indirectly by the substituent R₁ in aromatic ring attached to the pyridone nitrogen. While for the molecules **2** the variable aromatic residue is introduced directly to the proton acceptor group C=NAr. In this case by varying the electron nature of the R₂ substituent in the aromatic ring, it is possible to change the electron density of the proton-acceptor group thus influencing the H-bond strength.

The ^1H NMR spectra in CDCl_3 and DMSO-d_6 revealed chemical non-equivalency of the primary amide group protons of these compounds that was shown to be caused mostly by intramolecular hydrogen bond formation between the amide proton and the pyridone carbonyl group. The chemical shift of the H^a proton that can form intermolecular hydrogen bonds with solvent molecules or with another amide molecule depends significantly on external factors such as solvent nature and concentration. At the same time the chemical shift of the H^b proton greater depends on such internal factor as electron nature of substituent R. At the same time the chemical shift of the H^b proton strongly depends on such internal factor as electron nature of substituent R. Moreover, the substituent influence on the H^b proton is more effective in deuteriochloroform medium than in DMSO-d_6 where the intramolecular hydrogen bond is less stable. The value of $\Delta\text{H} = \delta(\text{H}^b) - \delta(\text{H}^a)$ could probably be applied as a simple comparative spectral index of the intramolecular hydrogen bond strength in these and similar compounds.

Keywords: intramolecular and intermolecular hydrogen bond, ^1H NMR chemical shifts, solvent influence, concentration influence, substituent influence

P-A 21: A comparative study of C-X... π halogen and C-H... π hydrogen bonding

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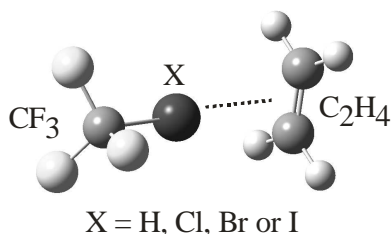
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The non-covalent interaction between a halogen atom (Lewis acid) and an electron rich region in a Lewis base is referred to as a "halogen bond" to stress the similarity with the better known hydrogen bond [1]. This electron rich region can either be a lone-pair of an atom such as nitrogen, oxygen, ... but it can also be a π -system of an aromatic or non-aromatic molecule. Even though these C-X... π interactions (with X=I, Br or Cl) are often overlooked when talking about halogen bonds, they do play an important role in crystal engineering [2] and in several biological systems [3, 4].

In order to gain more insight into the C-X... π interactions, we have studied the formation of weakly bound molecular complexes between the trifluoromethyl halides CF₃I, CF₃Br and CF₃Cl as Lewis acids and benzene, propene and ethene as Lewis bases dissolved in liquid argon and in liquid krypton, using Raman and FTIR spectroscopy. Structural and spectral information on the complexes was obtained from ab initio calculations at the MP2/aug-cc-pVDZ-PP level. Conversion of the ab initio complexation energies into complexation enthalpies was achieved by applying Monte Carlo Free Energy Perturbation (MC-FEP) calculations in order to correct for solvent influences and statistical thermodynamics to account for thermal and zero-point vibrational contributions. The resulting values were compared with the experimental data deduced from the cryosolutions, which show that for all halides C-X... π halogen bonded complexes are formed. Using spectra recorded at different temperatures, the complexation enthalpies were determined.

To increase the knowledge about the differences and similarities between halogen and hydrogen bonding, we have performed similar studies on the hydrogen bonded complexes between CF₃H and the aforementioned Lewis bases. The properties of the C-H... π hydrogen bond and these of the equivalent characteristics of the C-X... π halogen bond are compared.



Keywords: C-X... π halogen bond, C-H... π hydrogen bond, cryosolution, Raman, FTIR, ab initio calculations

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P-A 22: Hydrogen bond in bis-quinolizidine salts

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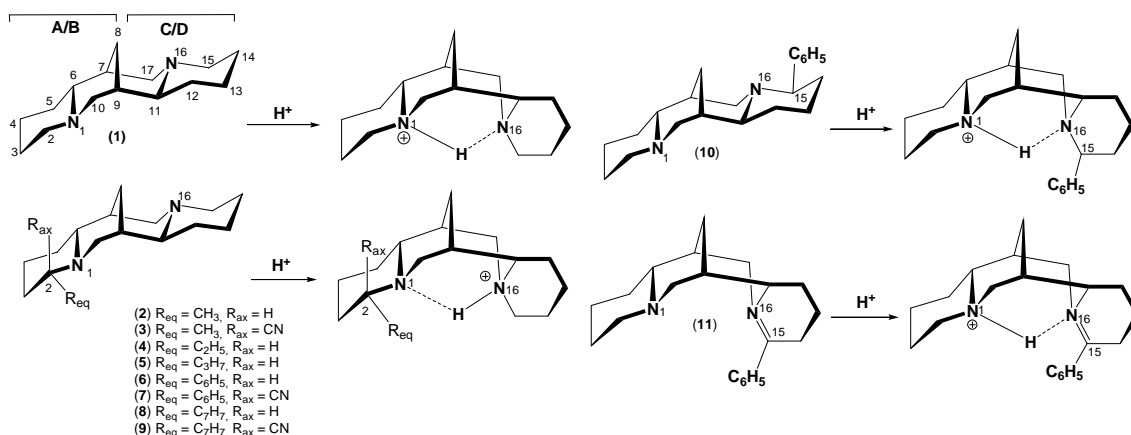
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Sparteine (**1**) and its derivatives have been of great interest due to their biological and biochemical significance. The crystal structure of the free base of sparteine has not been determined, as in the free state it occurs only as an oil. However, the structures of certain sparteine derivatives have been determined by X-ray analysis. All C2 saturated derivatives: 2-methylsparteine (**2**), 2-cyano-2-methylsparteine (**3**), 2-ethylsparteine (**4**), 2-isopropylsparteine (**5**), 2-phenylsparteine (**6**), 2-cyano-2-phenylsparteine (**7**), 2-(p-tolyl)sparteine (**8**) and 2-cyano-2-(p-tolyl)sparteine (**9**) have the *trans* configuration and boat-chair conformation of the C/D fragment. The same configuration occurs in 15-phenylsparteine (**10**) and 14-dehydro-15-phenylsparteine (**11**) occurs in a *trans* A/B *cis* C/D (all-chair) system. All these compounds give monosalts very easily.

As follows from X-ray and spectroscopic data, in crystalline sparteine-H⁺ the proton is located exclusively on N1 [1]. It was proved that in the case of sparteine molecule, the passage from solid to solution (CD₃CN) is accompanied by prototropy, giving rise to tautomeric equilibrium, in which the form with a proton located on N16 predominates. In C2 substituted sparteines only the N16 atom is protonated. As a consequence, an intramolecular hydrogen bond is formed with simultaneous inversion of the configuration at the N16 atom [2-4]. The strength of the intramolecular hydrogen bond should be correlated with the basicity of the corresponding free bases: higher basicity should be accompanied by a shorter N1...N16⁺ distance. Introduction of a cyano group with a negative induced effect into C2-substituted sparteines significantly reduces the basic properties of the nitrogen atom N1, which should result in a weaker hydrogen bond in cyano derivatives.

In contrast to C2 sparteine derivatives, upon the reaction of **10** and **11** with HClO₄, nitrogen atom N1 is protonated and an intramolecular hydrogen bond is formed [2].



Keywords: sparteine, sparteine derivatives, monoprotonated salts, hydrogen bond

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P-A 23: The structure of water confined at the proximity of a hydrophilic and a hydrophobic surface, x-ray diffraction study

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The X-rays diffraction study of the structure of confined water in two silica gel samples has carried out. The first sample is non-modified whose essentially hydrophilic and the second one is modified whose presents a predominately hydrophobic state by a grafting a trimethyl groupments at her internal surface by a specific chemical treatments [1]. The pair correlation function of water confined in silica gel powder non-modified and the modified one shows that the water molecules structure depends on the contribution amount of the water-matrix interaction. In fact, it appears that the water confined on the non modified sample presents a reorganization of water's molecules at the second neighbor's level due to the distortion or and brokenness of the hydrogen bonding. The second peak, at 4,5Å in the bulk water, is decorrelated in two peaks at 4 and 4,8Å. However, in the modified silica gel sample, a more restructuration at the second neighbors is found and a new peak at 3,6Å is found precisely at a distance where the probability of close neighbors is the lowest in the bulk water, it may be attributable to non-bonding water-water bonding.

Keywords: water confined, X-rays, silica gel, hydrophilic, hydrophobic

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P-A 24: Hydrogen bonds in self- and heteroassociates of cumyl hydroperoxide in solutions and polymeric matrixes

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FTIR spectroscopy is widely used for the research of hydrogen bonds AH...B in solutions when AH and B concentrations are not more than 0.1-0.2 mol/l. In this case, isolated AH molecules, AH...H and AH...B dimers (self- and heteroassociates) take place in the solutions. When AH and B concentrations are higher, the more complex associates appear. It makes difficulties for the interpretation of the FTIR spectra and for the use of FTIR spectroscopy consequently. So, the development of computer technologies and mathematic treatment of experimental data is actual problem. It will allow us to extend the range of problems which are resolved by FTIR spectroscopy in the field of hydrogen bonds and the analysis of complex mixtures too.

In this work a new approach in study of AH...H and AH...B associates by FTIR spectroscopy, which is combined with the factor analysis (FA), is proposed. Cumil hydroperoxide (CH₃)C₆H₅COOCH (CUN) was considered as an AH, acetone (AC), acetophenone (AP) and acetonitrile (AN) were considered as acceptors B, n-decane was a solvent. CUN concentrations varied in the range of 0.01-0.22 mol/l. AC, AP and AN concentrations were 0.19, 0.22 and 0.5 mol/l, respectively. FTIR spectra were registered in region of 3000-3700 cm⁻¹ in temperature interval of 20-85°C.

The use of FA methods proposed by us earlier [1,2] and developed in present work has allowed to determine a number of self-(dimers (D), trimers (T) and heteroassociates (monomer (M)+acceptor (B)) in the solutions of different concentrations, to obtain the spectra of associates and their concentrations (C), to define the equilibrium constants and thermodynamic parameters of hydrogen bonds formation. The j-solution components concentrations were shown to satisfy to the material balance equation:

$$(C_M)_j + 2(C_D)_j + 3(C_T)_j + (C_B)_j + 2(C_{B+M})_j + 2K_D(C_{B+M})_j [2(C_M^0)_j^2 - (C_{B+M})_j] + 3K_T(C_{B+M})_j [3(C_M^0)_j^2 - 3(C_M^0)_j(C_{B+M})_j + (C_{B+M})_j^2] = (C_{CUN}^0)_j + (C_B^0)_j,$$

where C_{CUN}⁰ and C_B⁰ are initial CUN and acceptor concentrations, respectively, K_D and K_T are the constants of CUN dimerisation and CUN trimerisation, respectively. The influence of different solvents and glassy polymeric matrixes on the band of OH stretching vibrations was compared.

Keywords: hydrogen bond, FTIR spectroscopy, factor analysis

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P-A 25: Density functional theory study of H-bond in self- and heteroassociates of cumyl hydroperoxide

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Cumil hydroperoxide forms many types of self- and heteroassociates with different structure because of availability of many axes of internal rotation and two oxygen atoms. The determination of the structure and type of associates in solutions by spectral investigations only is difficult. We have carried out the quantum chemical calculations of energy and vibrational spectra of different conformations of cumil hydroperoxide (CH₃)₂C₆H₅COOCH (CUN), dimers and trimers of CUN and different heteroassociates CUN with acetone (AC), acetophenone (AF) and acetonitrile (AN). The calculations were carried out by using the density functional theory (B3LYP) on the basic set 6-31G with inclusion of the d-type polarization functions for nonhydrogen atoms and p-type polarization functions for hydrogen atoms (6-31G(d, p)). The basic set 6-311++G(df,p) was used for the calculations of CUN+AN heteroassociates. All calculations were performed by means of the GAUSSIAN 98 package of quantum chemical programs.

The geometric structures were found by the optimization of geometric parameters. The calculated structure stability was determined by an absence of negative values of calculated vibrational frequencies.

The comparison of the calculations carried out with the experimental investigations of FTIR absorption spectra have allowed to establish the structure of CUN self- and heteroassociates. Relative energy of hydrogen bonds in CUN heteroassociates has been determined.

The calculations of CUN+AC associates have shown that the frequency of stretching OH vibration of CUN molecule hydrogen bonded with AC molecules is lower than the calculated frequencies ν_{OH} of associate CUN+AF. This fact is really observed from the results of the factor analysis of the experimental spectra of CUN +AC and CUN +AF solutions. The calculated values of hydrogen bonds energy of heteroassociates are in good agreement with the results of FTIR spectroscopic investigation.

Quantum-chemical calculations were carried out at SCCU of Kazan Scientific Center of RAS.

Keywords: hydrogen bond, DFT calculations, cumil hydroperoxide

P-A 26: Structures, spectroscopy analysis and DFT calculations of gemini betaine hydrates

Iwona Kowalczyk

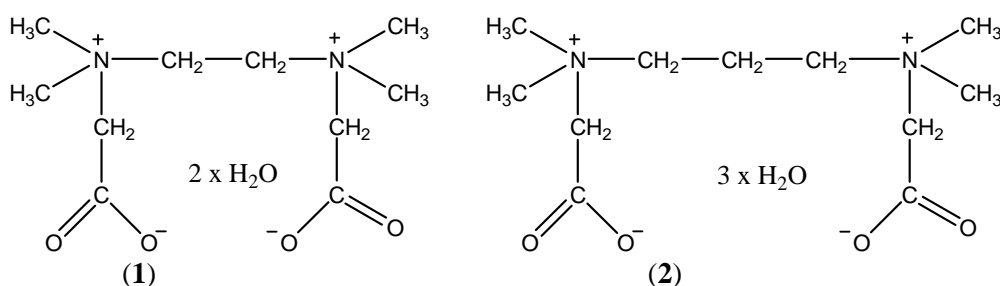
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A gemini betaines comprises two betaine moieties in the same molecule and accordingly possesses pairs of carboxylate groups and quaternary ammonium or pyridinium moieties [1,2]. Recent studies have shown that a double betaine which comprises pairs of ammonia and carboxylate moieties in the same molecule, exhibit interesting features with regard in the mode of hydrogen bonding and molecular packing.

The results indicate that betaine compounds are good proton acceptors and the carboxy oxygen atoms easily form acceptor hydrogen bonds involving the hydrogen atoms of the water molecules and the hydrochlorid and hydrobromic acids. Betaines have a variety of applications as microbiocides, therapeutic agents and surface active compounds [3].

The use of microbiocide of the same type for a long time may cause an increase of resistance of microorganisms which is a very serious problem. To avoid this problem structures and types of microbiocides have to be continuously changed [4,5].

In the present study, two flexible double betaines are synthesized, N,N'-dicarboxymethyl-N,N,N',N'-tetramethylethylenediammonium dihydrate (1) and N,N'-dicarboxymethyl-N,N,N',N'-tetramethyl-1,3-propanediammonium trihydrate (2).



The effect of water molecules on the structure, conformation and hydrogen bonds of the gemini compounds in crystals and solutions were studied by FTIR, ^1H and ^{13}C NMR spectra and B3LYP calculations and compared with results of X-ray diffraction.

Keywords: Gemini betaines, FTIR, ^1H and ^{13}C NMR, DFT calculations

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P-A 27: Argon matrix shift in the OH stretching fundamental of n-propanol: a combined experimental and quantum chemical nanocoating study

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Supersonic jet Raman spectroscopy [1,2] reveals an increasing bathochromic shift of the OH stretching vibration in the most stable conformation of propanol with increasing extent of argon nanocoating [3,4]. It falls short of the bulk matrix limit of 17 cm⁻¹ even at large nozzle distances. Quantum chemical harmonic frequency calculations [4,5] up to the CCSD(T) level show that this shift cannot be accounted for by individual Ar atoms or even a first solvation layer, but instead requires several layers of Ar atoms around the molecule to be explained. It is shown that the stability of Ar-propanol clusters correlates with the number of close O and C contacts to the Ar and that bathochromic shifts are largely caused by backbone solvation, whereas OH solvation tends to increase the OH stretching frequency. The results shed some light onto extremely weak hydrogen bonds between OH groups and rare gas matrix atoms.

Keywords: Raman spectroscopy, MP2-R12, supersonic jet expansion, weak hydrogen bonds

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P-A 28: Anharmonic vibrational calculations and matrix isolation experiments on the H₂O...CO complex

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Molecular complexes picturing hydrogen bonding are very common in molecular science and prevalent, for example, in atmospheric chemistry, catalytic reactions, surface chemistry, material science, and biological processes. The hydrogen-bonded complex between water and carbon monoxide is one of the interesting complexes in atmospheric chemistry and its processes.

Quantum chemical calculations have been shown to be a valuable tool to study the nature of hydrogen-bonded complexes. Calculations indicate that the 1:1 complex between water and carbon monoxide exhibits two stable structures, i.e. HOH...CO and HOH...OC.[1-3] In all these studies the carbon attached H₂O-CO complex is the most stable configuration and it has also been characterised thoroughly in the gas phase and in the matrix.[4-8] The other stable complex structure, where the oxygen atom of CO is pointing towards the OH bond of water has been identified only in low-temperature Kr and Xe environment.[6,7]

Here, the vibrational properties of the two complex structures were studied by harmonic and anharmonic vibrational calculations, which were combined with matrix isolation infrared experiments in the spectral region of 7500-500 cm⁻¹. The anharmonic calculations were performed with the cc-VSCF method based on MP2-computed intermolecular potential energy surface. Besides the fundamental transitions, the cc-VSCF calculations were used to predict combination and overtone transitions and their intensities. Calculations at the MP2/aug-cc-pVTZ level of theory indicate that both H₂O-CO and H₂O-OC complexes have a rich overtone and combination spectra. Consequently, several new overtone and combination bands of the H₂O...CO complex and its isotopologues are reported and assigned. The performance of the cc-VSCF calculations of all the observed transitions involving exclusively intramolecular modes is very good (relative shift of 2-4%).

Keywords: water, CO, matrix isolation, anharmonic calculations, overtones

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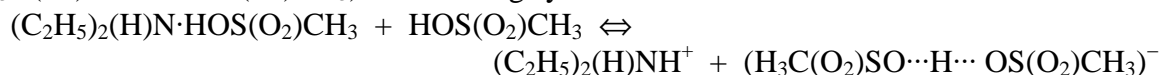
P-A 29: Ion-Molecular Interactions and Ions with Strong Symmetric H-Bond in Solutions of Methanesulfonic Acid in Diethylamine

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Non-aqueous solutions of strong acids are efficient catalytic systems, whose activity is determined by the compositions and structure of proton-containing species. A fundamental property of protons in solution is the formation of ions and complexes with strong symmetric H-bond [1]. The formation of noncharged 1:1 complexes with strong quasisymmetric H-bond is typical for many nonwater acid-base systems [2]. We have a considerable amount of information on systems with (OH...O) – bonds. Complexes formed by H-bonds between nitrogen and oxygen atoms are studied much fewer. The aim of this investigation was to study the acid-base interaction in the solutions of the methanesulfonic acid (MSA) in diethylamine (DEA) due to Multiple Attenuated Total Reflectance (MATR) IR spectroscopy. Components are completely associated to 1:1 complexes at equimolecular ratio solutions. The IR-spectrum of such a complex dramatically differs in the spectra of original components: MSA and DEA. Under the acid excess, molecule of MSA tears the anion away from 1:1 complex and forms the negative charged ion $(\text{H}_3\text{C}(\text{O}_2)\text{SO}\cdots\text{H}\cdots\text{OS}(\text{O}_2)\text{CH}_3)^-$ with strong symmetric H-bond:



Under the DEA excess, complexes 1:1 preserve their structure and are not solvated by the base molecules, i.e., the solution is divided into two layers: the 1:1 complex and the pure DEA.

This work was financially supported by the Russian Foundation for Basic Research (project no. 08-03-00361).

Keywords: H-bond, acid-base interaction, IR-spectra

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P-A 30: Interrelation between intramolecular hydrogen bond, steric effects and π electron delocalisation in nitroanilines

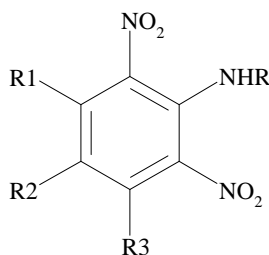
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Structures of the series of sterically crowded nitroanilines have been optimised using B3LYP method at 311++G** level. Geometric parameters of the optimized structures have been compared with the experimental values [1].



R = Ph, Me, H

R1 = NHR, NO₂, H

R2 = NO₂, H

R3 = Me, CF₃, Cl, H

The competitive effects of the intramolecular hydrogen bonds formation and steric effects on the π electron delocalisation and conformation of the studied molecules have been discussed using aromaticity index HOMA, the NBO and AIM analysis. For comparison, the calculations for analogues compounds without intramolecular hydrogen bonds have been done.

Keywords: Nitroanilines, intramolecular hydrogen bond, steric effect

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P-A 31: Percolation analysis of the hydrogen bond networks in water coloured with respect to hydrogen bonds lifetimes: computer simulation

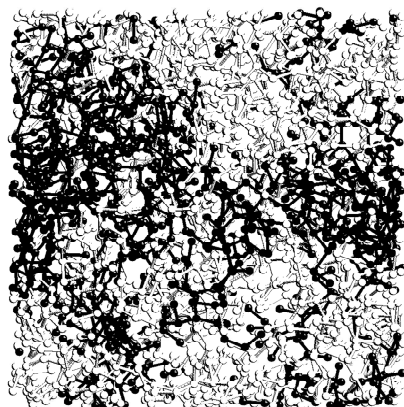
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According to commonly accepted notion the infinite three-dimensional network of hydrogen bonded network exists in liquid water. Nods or bonds of this network can be coloured with respect to various properties: pair energies (bonds), total potential energies, Voronoi polyhedra volumes and tetrahedrality indices (nods, that is to say, molecules). In our earlier works it was shown that nods or bonds with high or low values of the parameters according which the network is being coloured group together forming ramifying clusters. Percolation thresholds for such colouring were determined (see for the review [1]). In this work we present the results of colouring water hydrogen bonded network with respect to hydrogen bond life-times. To this end molecular dynamics trajectories (3456 molecules in the simulation box with periodic boundary conditions, virtual temperature 261 K and 297 K) were recorded and hydrogen bond lists were made for the recorded configurations. A configuration was chosen and its hydrogen bond list was compared with such lists of the series of the preceding and subsequent configurations. As trajectories were rather long, about one hundred configurations could be chosen for each temperature. Hydrogen bond life-times were determined for the chosen configurations; their hydrogen bond networks were coloured according these life-times and percolations analyses was performed. Average percolation threshold is about 20 ps for 261 K and about 8 ps for 297 K. Values of percolation thresholds are close to average total hydrogen bond life-times for the same temperature. As numbers of bonds and nods in coloured clusters are close to each other, it means that degree of ramification in them is rather low.



Colouring of one of the configurations (T=261 K). Percolation threshold is 18 ps for this configuration. Bonds with life-times longer than 19 ps are coloured (gray). They form 402 finite clusters. Two of them are shown in black: the largest one (885 molecules) and a cluster, containing 154 molecules.

Keywords: Hydrogen bond network, hydrogen bond life-time, percolation threshold

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P-A 32: Hydrofluoric acid spontaneous dissociation : keeping pace with electrons

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The extent of charge transfer between the electron lone pairs of water (H₂O) and the anti-bonding orbital of hydrofluoric acid (HF) may determine the strength of their hydrogen bonding interaction and even trigger ionic dissociation of the acid in aqueous solutions. We used cryogenic hydrofluoric acid solutions prepared as thin films in UHV by simultaneous vapour deposition with two molecular beams on Pt(111) at 50K as model systems. Reflection-absorption infrared spectroscopy allowed us to probe the complex nuclear dynamics along the proton transfer reaction coordinate. The observation of a Evan's hole near 1850cm⁻¹ reveals a strong coupling between the HF H-bonded donor stretching and the H₂O H-bond acceptor bending intramolecular vibrations in the amorphous solids. Assuming heterogeneous broadening of the HF stretching mode, we analyzed the Evan's hole using a two-level model vibrational Hamiltonian to extract the anharmonic coupling between these two modes. The strength of this coupling was interpreted using electronic structure calculations to estimate the contribution from dipole-dipole coupling while Natural Bond Orbital analysis gave insight into the charge transfer contribution. These results when compared to experimental value allowed us to evaluate the respective contributions from charge transfer and dipole-dipole couplings. Finally, ongoing ultraviolet photoelectron spectroscopy (UPS) studies of cryogenic mixtures of HF in amorphous solid water (ASW) will be presented providing further evidence of charge transfer between the this weak acid and water.

Keywords: Hydroge fluoride, charge transfer, spectroscopy

P-A 33: Complexation-induced stabilization of higher-energy *cis* conformer of formic acid

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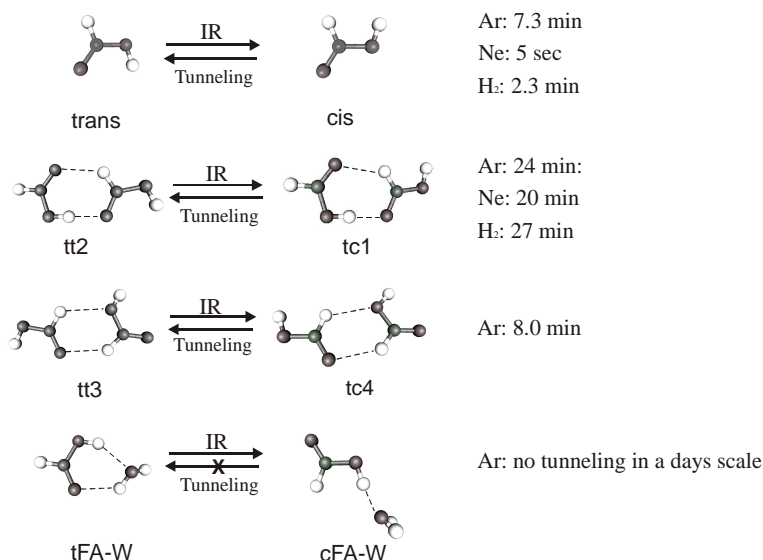
Two conformers of formic acid (FA) differ by orientation of the OH group. The high-energy *cis* conformer (cFA) decays into the *trans* form (tFA) via hydrogen quantum tunneling. This process has been studied in rare gas matrices [1]. The stabilization of *cis*-FA can be done in hydrogen-bonded complexes where back *cis-to-trans* process is slowed down. In the present work, we describe the preparation and kinetic properties of FA dimers and water complexes in rare gas matrices.

The *cis*-FA, *trans-cis* dimers and *cis*-FA-water complexes are produced by light-induced rotation of the free OH bond of the corresponding *trans* forms.

The tunneling kinetics in two *trans-cis* dimers (tc1 and tc4) is measured in argon, neon and hydrogen matrices. The decay rate of tc1 is found practically independent on temperature and matrix. The decay rate of tc4 at 8 K in solid argon is close to that of *cis*-FA monomer but it increases more slowly with temperature [2, 3, 4].

First experimental identification of the *cis*-FA and water (cFA-W) complex is done. The long-term stability of this complex is observed – no back tunneling of cFA-W in scale of days is detected [5].

Thus, it has been demonstrated that the *cis-to-trans* process can be efficiently suppressed by hydrogen bonding between cFA and other molecules.



Keywords: hydrogen bond, formic acid, conformational change

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P-A 34: Multidimensional Quantum Dynamics of Carboxylic Acid Dimers

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Due to their prototype character, carboxylic acid dimers have been in the focus of experimental and theoretical studies for decades. From the theoretical point of view, the quantum nature of the hydrogen and the strong coupling between its motion and that of the molecular framework lead to multidimensional quantum dynamics.

Here various aspects of the theoretical simulation of vibrational and vibrational-rotational-tunneling spectra will be discussed. First, on the specific example of formic and acetic acid dimers we will show how the broad stationary absorption OH-stretching bands can be understood in terms of multiple conformers and multidimensional anharmonic vibrational dynamics [1,2]. Next, the focus will be on the hydrogen tunneling motion. The recently developed general approximation to the reaction path (GARP) method will be presented and applied to the description of the double proton transfer reaction in the formic acid dimer isotopologues [3,4]. We will address questions such as: Does vibrational excitation promote H-tunneling? Which molecular motions are important for the understanding of tunneling motion in the formic acid dimer? Does isotope substitution affect the mechanism of H-transfer.

Keywords: Carboxylic acid dimers, tunneling spectra, vibrational dynamics

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P-A 35: FTIR cryospectroscopic studies of the weakly H-bound ClH...FCD₃ complex

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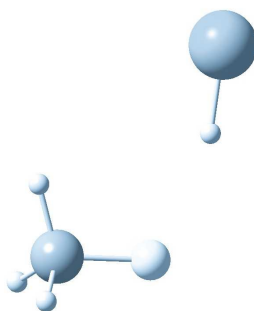
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FTIR spectra of HCl/FCD₃ mixture dissolved in liquefied Kr were studied in 400 ÷ 7000 cm⁻¹ frequency domain in temperature interval 120÷170 K. The effect of weakly H-bound ClH...FCD₃ complex formation on the fundamental and overtone bands of proton donor and proton acceptor counterparts have been carefully examined taking into account vibrational resonances [1]. Information on the enthalpy of the complex formation $\Delta H \sim (2.56 \pm 0.04)$ kcal/mol has been obtained by studying the temperature variations of relative intensities of selected bands ascribed to the monomers and complex. The respective theoretical value has been found is in reasonable accordance with the experimental result.

Theoretical calculations were performed using the GAUSSIAN 03 Rev. C.02 program. CCSD ab initio calculations have been carried out with the Pople-type 6-311++G(3df,3pd) basis set. The equilibrium geometries, interaction energies and harmonic vibrational frequencies of the complexes were obtained using CP-corrected gradient techniques. The theoretically predicted global minimum corresponds to geometry shown on the figure:



Potential energy and dipole moment surfaces as functions of the corresponding normal coordinates have been obtained by ab initio grid calculations and then used in prediction of the IR spectrum of HCl proton donor in the overtone region.

The work was supported by RFBR (N 08-03-00615) grant.

Keywords: Hydrogen bond, HCl, anharmonicity

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P-A 36: Anesthetics at Work: The complexes of halothane with benzene(-d₆)

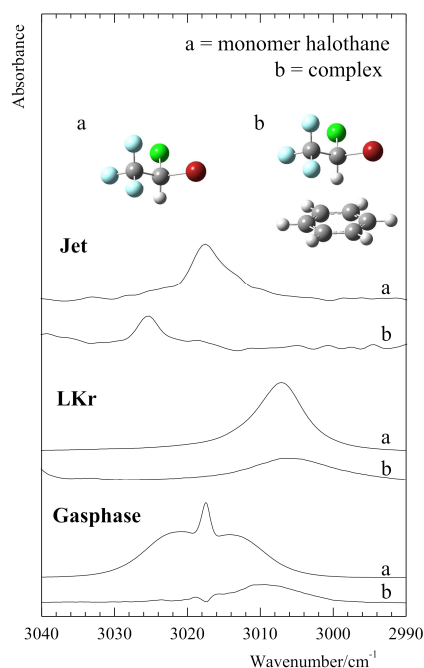
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Although anesthetics are used daily all over the world a lot is still unknown about their mechanisms and interactions [1]. To gain more insight in this matter the formation of C–H··· π bonded complexes between halothane and benzene(-d₆) was studied. To this end infrared and Raman spectra of mixtures of halothane and benzene(-d₆) have been investigated in liquid krypton, in supersonic jet expansions and in the gas phase at room temperature. The formation of complexes between halothane and benzene(-d₆) with a 1:1 and 2:1 stoichiometry was observed as before [2-3]. The complexation enthalpy in liquid krypton amounted to -9.8(2) and -16.3(3) kJ mol⁻¹ respectively. The stretching mode of the C–H bond involved in the formation of the complex was observed to blue shift by 7.7(10) cm⁻¹ in the jet. However in solutions of liquid krypton and at room temperature a small red shift was observed. These experimental results are compared with ab initio calculations at the MP2, B3LYP and CCSD(T)/aug-cc-PVDZ level.



Keywords: Halothane, C–H··· π hydrogen bond, FTIR, Raman, cryosolution, supersonic jet

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P-A 37: The role of hydrogen bonding in aqueous radical salvation via ultrafast X-ray absorption spectroscopy

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The study of the behavior of free inorganic radicals in water has recently attracted a lot of interest in conjunction with a rising environmental awareness. It has already been emphasized the role played by free radicals such as bromine or chlorine in ozone depletion. In drinking and cooling water treatment, the reaction with chlorine, chloramines, chlorine dioxide or hydrogen peroxide can cause problems when the oxidants are used in combination with ozone. Because inorganic species, such as hydrated halogen atoms, tend not to produce strong colors under ultraviolet light, it is difficult to study their structure and reactions using conventional spectroscopic methods. Transient X ray absorption spectroscopy has proven to be a useful tool to investigate the hydration of one of these short-lived species – the bromine atom. Using the laser pump x-ray probe capabilities of XOR beamline 7-ID at the Argonne Advanced Photon Source, new experimental evidence for the behavior of hydrated bromine radicals has been found. These new insights could open up studies of other inorganic species of relevance for atmospheric and oceanic species, in interstellar chemistry as well as general inorganic chemistry research.

This work was supported by the U. S. DOE Office of Basic Energy Sciences under contract # DE-AC02-98CH10886.

Keywords: 7-ID XOR, material science, atomic physics, chemistry, time resolved x-ray scattering, time resolved x-ray absorption fine structure

P-A 38: Vibrational Spectroscopy of Small Water/Alcohol Clusters

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Water/alcohol mixtures exhibit several physical anomalies which were extensively studied on the macroscopic scale [1]. To rationalize the origin of these peculiarities a fundamental understanding of their microscopic properties like the constitution and conformation of small clusters is crucial. In this context, mixtures of water with methanol or ethanol are the simplest and most interesting model cases which are accessible to accurate quantum chemical investigations. Ethanol represents the first case where internal conformational degrees of freedom influence the cluster formation.

In this study we prepare and isolate mixed dimers and trimers in supersonic jet expansions at low temperatures and investigate them by spontaneous Raman spectroscopy [2]. FTIR spectra assist the assignment due to partially complementary selection rules [3, 4].

Thus, we are able to prove that water takes the role of a hydrogen bond donor in the mixed water/alcohol dimers [5]. Furthermore we can show that the mixed water/ethanol dimer prefers ethanol in a gauche conformation as the hydrogen bond acceptor although this is not the most stable conformation in the isolated ethanol molecule. This represents a simple case of adaptive aggregation. In mixed trimers a strongly negative mixing enthalpy, a property well known from bulk solutions [6, 7, 8], is also reflected on the microscopic scale.

Keywords: infrared spectroscopy, water, clusters, methanol, ethanol, jet, complexes, expansion

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P-A 39: Hydrogen bonds affecting M-OH₂ strength in lanthanide complexes

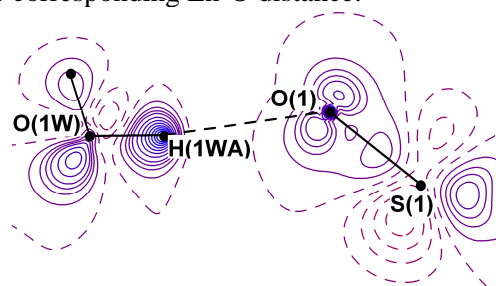
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Lanthanide complexes are of special interest as effective luminescent materials [1] and contrast agents for magnetic resonance imaging (MRI) [2]. In both cases, the lanthanide to water binding (Ln-OH₂) is an important aspect. For instance, the major parameter being responsible for the sensitivity of lanthanide complexes is the rate of water exchange, directly related to the Ln-O bond strength [3]. Recently it was shown that the Ln-OH₂ distances vary in accordance with the difference in H-bonded pattern [4]. Hence, it is of paramount importance to check if namely the hydrogen bonds determine the lanthanide to water binding or vice versa. As a subject of investigation crystalline nonahydrates of lanthanide (III) triflate, where lanthanide is neodymium, europium, and terbium, were chosen due to the distinct difference between Ln-O bond lengths for axial and equatorial water molecules, which should be related to their different involvement into intermolecular contacts [5].

To analyze the role of H-bond formation in the lanthanide to water binding we have carried out the topological analysis [6] of the electron density distribution functions in the above crystals. This approach gives the opportunity to fetch out the bonding interactions and to estimate their energy from the X-ray diffraction data [7]. Obtained results allowed demonstrating that, despite the weakness of hydrogen bonds relative to that of the Ln-O interactions, the former have a decisive influence on the chemical binding within the Ln(H₂O)₉ moiety in all the studied complexes. Indeed, the stronger the H-bonds with the water molecule are, the smaller is the change in the corresponding Ln-O distance.



This is the first experimental observation of the intermolecular interactions with the outer-sphere species governing the binding of lanthanide cation with the first coordination shell. Therefore, careful examination of the supramolecular patterns, especially H-bonded ones, is a crucial aspect for the directional design of luminescent materials and MRI contrasting agents.

Keywords: lanthanide to water binding, H-bonds, topological analysis

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P-A 40: Raman spectroscopy of formic acid monomer and dimers in matrices

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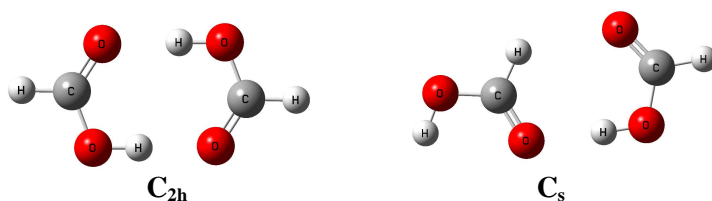
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Formic acid (FA) is the smallest carboxylic acid that is of considerable interest in atmospheric chemistry and in biological context. This is one of the simplest models showing trans-cis rotational isomerism. In the gas phase FA exists primarily in trans-form, the higher-energy cis-form being less abundant [1].

Formic acid homodimer can form a variety of hydrogen bonded structures. This offers a representative example to study properties and reactions of systems involving the C-H...O and O-H...O noncovalent interactions. In the gas phase, FA molecules aggregate preferably to form cyclic structure of C_{2h} symmetry, consisting of eight-membered ring with two equivalent C=O...H-O hydrogen bonds. This structure is known to be one of the most stable neutral complexes, and its complexation energy has been theoretically determined to be $\cong 63 \text{ kJ mol}^{-1}$. The less stable acyclic dimer has been detected so far in the IR spectra of the FA isolated in low temperature matrices [2,3] as well as in helium nanodroplets [4].

Here, we present first Raman spectra of the formic acid monomer and its dimers isolated in low temperature argon matrices. Nine fundamentals of the HCOOH monomer were identified and additionally the OH torsion overtone engaged in Fermi resonance with the COH bending was observed. Ten Raman active symmetric modes of the cyclic (C_{2h}) dimer were detected and assigned. The experimental results confirm also the formation of the open dimer of the C_s symmetry. Six fundamental transitions were identified for this form.

A detailed analysis of the low frequency region allowed identification of all three bands related to the inter-monomer motions of the cyclic dimer and one band of the open structure. The experimental results are compared with computed Raman spectra obtained at the B3LYP/6-311++G(2d,2p) level yielding a very good agreement between theoretical anharmonic and experimental spectra.



Keywords: Raman spectra, formic acid, hydrogen bonded complexes, low temperature matrices

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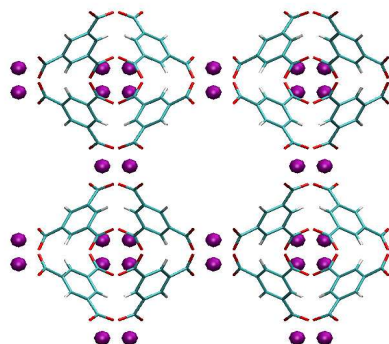
P-A 41: Influence of water on adsorption in Metal Organic Frameworks (MOFs) – A Molecular Simulation study

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Copper Benzene tricarboxylate (Cu-BTC) is a MOF with an electrically neutral framework, which is composed of dimeric cupric tricarboxylate units with a short Cu-Cu internuclear separation [1]. They are formed by primary building blocks connected to form a face centered cubic crystal framework, and secondary building blocks forming tetrahedron-shaped pockets accessible for small molecules through small windows.



In the present investigation, we have performed Grand Canonical Monte Carlo simulations study on H₂O adsorption in Cu-BTC using classical interatomic force fields. We have studied the effect of water molecules on CO₂ adsorption in Cu-BTC. Two sets of atomic charges are considered in our simulations, one from our earlier study i.e. from Snurr et al. Study and another from Calero et al. [2] Study. We have studied dehydrated Cu-BTC, Cu-BTC with 1H₂O and Cu-BTC with 48H₂O to determine the hydration effect in these systems.

Our studies indicate that, CO₂ replaces H₂O at higher pressure and sensitive to convergence so that maximum number of Monte Carlo steps need to get the convergence. Adding one water molecule in the system slightly increases the CO₂ adsorption at the cage center and slightly reduces the CO₂ adsorption at window center in low pressure region. The CO₂ adsorption in Cu-BTC is higher when the water molecules are located at the Cu site than water randomly placed. From our study we have concluded that the force field parameters played important role in studying the adsorption isotherms of these system. Among 48 water molecules the Cu site, only 30 to 40 water molecules were located at the Cu sites. The remaining water molecules form clusters in the nanopores of the material.

Keywords: metal-organic frameworks, molecular simulation, adsorption

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P-A 42: The acidic and basic properties of formaldoxime

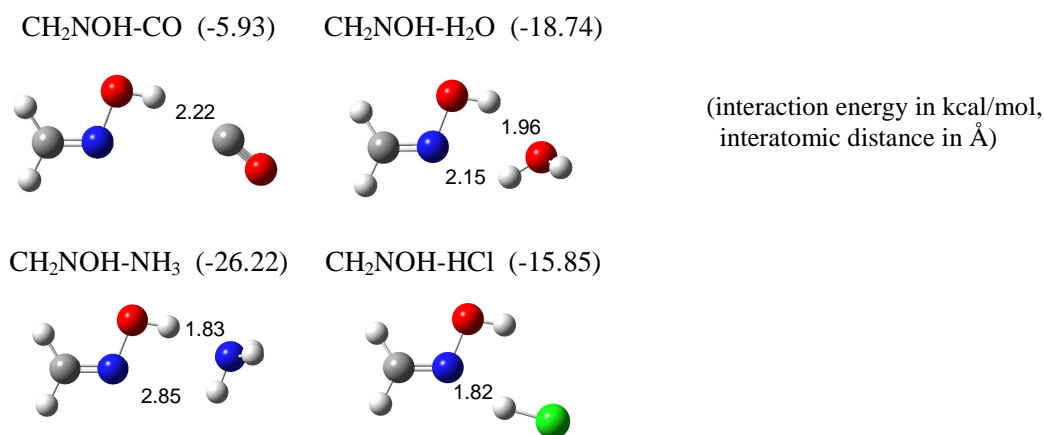
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Formaldoxime, a structural isomer of formamide, is the simplest member of the oxime family. This important class of compounds containing $>C=NOH$ group has numerous applications in industrial chemistry, pharmacology and biological research. The study of formaldoxime hydrogen bonding is attractive because of the variety of possible complexes it may form. The $>C=NOH$ group involves the (N)OH proton donor site and two strong acceptor sites: the nitrogen and oxygen atoms; all sites may become active when formaldoxime is interacting with various molecules. The electron - withdrawing effect of the hydroxyl group on the basicity of both nitrogen and oxygen atoms is also of interest.

Here we report the results of the FTIR and ab initio study of the formaldoxime complexes with water, ammonia, hydrogen chloride and nitrous acid isolated in argon matrices. The structures of the complexes trapped in the matrices are determined and the proton donor and proton acceptor abilities of the CH_2NOH are discussed. Both 1:1 and 1:2 complexes between formaldoxime and H_2O , NH_3 or HCl molecules are trapped in the matrices. The preferred basic site in formaldoxime 1:1 complexes is the nitrogen atom. The 1:2 complexes have seven-membered ring structures in which $(H_2O)_2$, $(NH_3)_2$ or $(HCl)_2$ dimers interact with the formaldoxime molecule. However, in the $CH_2NOH-(HCl)_2$ complexes the second HCl molecule may be attached to the oxygen site if the nitrogen atom is blocked. The basic and acidic properties of the N-OH group in formaldoxime and hydroxylamine are compared. The formaldoxime complexes tend to form preferentially the cyclic rather than the linear structures.



Keywords: formaldoxime, matrix isolation, molecular complex

P-A 43: Quantification of the energies of solvophobic effect and solute-solvent hydrogen bonds in associated solvents

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Thermodynamic functions of solute-solvent hydrogen bonding in associated solvents are difficult to determine using direct experimental methods. On the other hand, complicated equilibria of solvent associates and cooperative effects of hydrogen bonding cannot be correctly described by simple relationships. To calculate them, one needs to apply some sophisticated association models.

However, experimental thermodynamic functions of solvation contain a contribution of solute-solvent hydrogen-bonding energy (specific interactions energy). We suggest and apply a method to determine the magnitude of this contribution.

Our approach is based on the previously deduced equations [1] to calculate the Gibbs energy and enthalpy of nonspecific solvation. A feature of associated solvents are the so-called solvophobic effects that also influence thermodynamic functions of solvation ($\Delta_{solv}f$), so that $\Delta_{solv}f$ is the sum of contributions from nonspecific solvation, solvophobic effect, and specific interactions. We also had to find a method to determine the solvophobic effect contribution.

It should be noted that while the concept of the hydrophobic effect [2] taking place in water is widely used and quite well defined, more general concept of solvophobic effects have even no generally accepted definition. There must be a difference between just 'poor solubility' of some solute in some solvent and the solvophobic effect. It is clear that solvents like glycerol, hydrazine or formamide behave much like water: not just apolar solutes are very poorly soluble in them, but also micellization of amphiphilic surfactants can occur in these solvents at certain critical concentration, and more similarities are there.

A thermodynamic function-based approach to recognize and quantify solvophobic effects taking place in solutions in various hydrogen-bonded solvents is suggested. The most evident manifestation of the solvophobic effect are the deviations from extrathermodynamic relationships between solvation properties and solvent parameters. The contribution of the solvophobic effect into the thermodynamic functions of solvation is a part that cannot be described by parameter(s) of nonspecific solvent-solute interactions.

We show that solvophobic effects occur not only in solvents with three-dimensional network of hydrogen bonds, such as water or polyhydric alcohols. Less pronounced, but distinct manifestations are present in solutions in monohydric alcohols.

It was found that in different solvents the Gibbs energies of the solvophobic effect are linearly correlated with molecular volume of a solute. The slope of a line is dependent on a nature of solvent: it has the largest magnitude in water, less magnitudes in polyols and the least –in monohydric alcohols, successively decreasing from methanol to octanol.

Using these linear correlations and the above-mentioned equation, the Gibbs energies of hydrogen bonding of different solutes with different associated solvents have been calculated. The influence of solute and solvent nature and cooperative effects on bonding energies is discussed.

Keywords: solute-solvent hydrogen bonds, associated solvents, solvophobicity, hydrophobicity

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P-A 44: Volumetric Glass-to-Liquid Transition in Amorphous Ices

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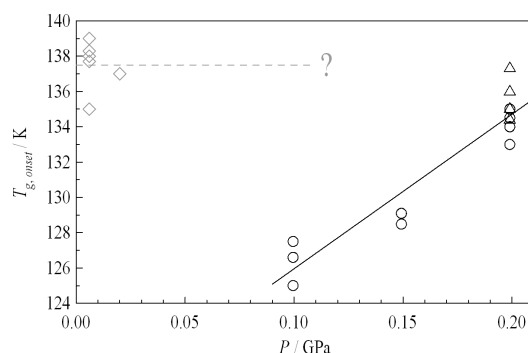
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Dilatometry experiments on amorphous ices at pressures up to 0.3 GPa are presented. The isobaric heating curves are followed using powder X-ray diffraction and interpreted in terms of three competing processes: the glass-to-liquid transition, irreversible relaxation and crystallization. We demonstrate the reversibility of the glass-to-liquid transition both for low-(LDA) and high-density amorphous ice (HDA). The onset for the volumetric glass-to-liquid transition $T_{g, \text{onset}}$ is determined to be ≈ 137 K for LDA \rightarrow LDL and ≈ 125 K (0.1 GPa) resp. ≈ 134 K (0.2 GPa) for HDA \rightarrow HDL [1]. Thus, the result for LDA is consistent with the 1 bar calorimetric data [2] and barely shifts with increasing pressure, whereas in case of HDA it increases by ≈ 90 K/GPa (see Figure) and crosses the crystallization line at $p \approx 0.3$ GPa.



In case of LDA the glass-to-liquid transition is very weak and becomes even weaker at increasing pressures so that it is difficult to locate the onset temperature. By contrast, in case of HDA the onset is easy to detect (unless crystallization precedes the onset). This is consistent with a “fragile” nature of the high-density liquid and a “strong” nature of the low-density liquid [3]. In addition we demonstrate that depending on preparation history structural defects, which result in early crystallization, may or may not be present in amorphous samples.

Estimates for the structural relaxation time are presented, which are obtained by keeping the sample under both isothermal and isobaric conditions for prolonged periods of time, where the process of structural equilibration is probed by powder X-ray diffraction and differential scanning calorimetry on quench-recovered samples. For instance at 130 K and 0.2 GPa the structural relaxation time in HDA is estimated to be roughly 800 seconds, which is consistent with the sample being slightly below its $T_{g, \text{onset}}$ (see Figure). By comparison, Mishima reports a T_g (not $T_{g, \text{onset}}$!) for emulsified HDA of ≈ 140 K at 0.1 GPa, which increases by about 50 K/GPa [4], which is in qualitative agreement with our findings. Andersson reports a dielectric relaxation time τ of ≈ 1 s and an ultraviscous liquid character of bulk HDA at 140 K and 1 GPa [5].

Keywords: amorphous ices, glass transition, relaxation behavior

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P-A 45: Detection of different states of water in porous silicon by IR spectroscopy

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Porous silicon (PS) is a good model object for studying new fundamental laws in the field of nanophysics, oxidation and the other chemical transformations in a silicon surface layer. It is known that the physical properties as well as adsorption properties of PS are a great extent associated with the state of its hydration coverage [1]. Water takes an active part in PS oxidation, which is important for temporal stability of PS characteristics. In our work we report the study of the different water states in PS samples subjected to various treatments by IR spectroscopy.

The samples of nanoporous silicon (with the pore size of 2-5 nm) were obtained by electrochemical etching of 10 Ohm-cm p-type (100) Si wafers. As-prepared sample was studied as well as the samples subjected to different treatments at room temperature (such as exposition to aqueous vapour and immersion in distilled H₂O) and vacuum annealing (10⁻² Pa) at 600 K. It was shown that the changes in the peak position and shape of OH stretching band during all treatments are observed. The position of this band varies between 2900 and 3550 cm⁻¹, which is concerned with variation of the energy of hydrogen bonds and water states in PS [2].

A considerable long-wave shift of OH stretching band compared to the band of bulk water is observed for the initial samples (see Fig. 1). The low frequencies of OH absorption band can be due to the absorbed Si^σ...OH₂^{+σ} (and also Si...H₃O⁺) complexes being, in turn, the sites for physisorption of water molecules. An increased acidity of surface site leads to strengthening the hydrogen bonds with surrounding water molecules and, correspondingly, to lowering of OH band frequency. Annealing at 600 K result in essential shift of OH stretching band maximum to higher frequencies (see Fig. 1). Vacuum annealing leads to water removal out of pores and partial desorption of hydrogen. As it is well known, water is adsorbed predominantly dissociatively onto the surface with great amount of unsaturated dangling bonds. This leads to formation of Si-OH species and subsequent physisorption of water on hydroxyls in the air.

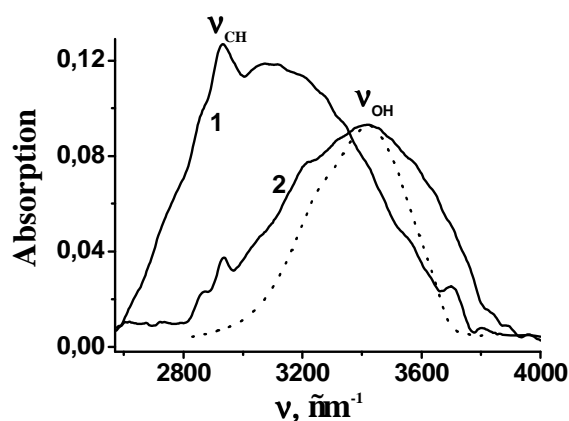


Figure 1. IR absorption spectra of initial porous silicon sample (1) and the sample annealed at 600 K and exposed to the air for 3 hour (2). For comparison, IR absorption band of distilled water is shown by dotted line

Exposition to aqueous vapour and immersion in distilled H₂O also cause to the short-wave shift of OH stretching band, which is assigned to decrease in HB energy.

Keywords: porous silicon, water, OH stretching band

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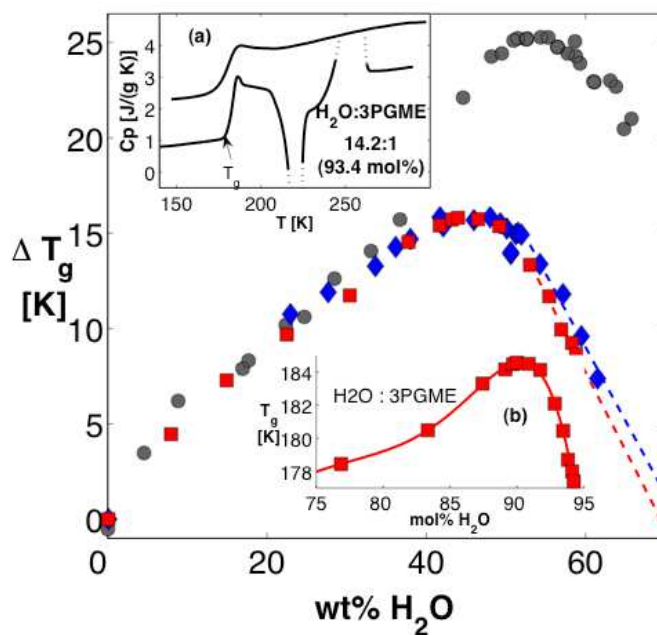
P-A 46: Anomalous concentration dependence of structural and water relaxations in aqueous solutions

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The hydrogen bonding interplay between water and other organic molecules control many material properties which are important both in nature and in a wide range of technological applications. Many macroscopic properties of H-bonded liquids are linked to the structural relaxation. To investigate the effects of H-bonding on the dynamics of complex materials, we focus on the structural relaxation and the secondary relaxation of water in binary aqueous mixtures using calorimetry, dielectric spectroscopy, quasielastic neutron scattering and neutron diffraction. When decreasing the H-bonding ability for a family of liquids, the concentration dependence of the structural relaxation time changes from a monotonic behaviour, as usually seen in mixed glass formers, to a remarkably non-monotonic variation. This anomalous behaviour suggests significant structural changes with composition. We quantitatively describe this phenomenon as a competition between two effects: (i) a H-bond induced formation of effective relaxing entities and (ii) a plasticizing effect due to the existence of "free" water. However, irrespectively of the different concentration dependence of the structural relaxations, we show that the water relaxations in the glassy state exhibit both qualitatively and even quantitatively similar behaviour. We discuss the results in terms of physical explanations to the quantitative relaxations times of water in supercooled, molecular aqueous solutions.



Keywords: supercooled liquids, structural relaxations, water relaxations

P-A 47: Can 2D IR spectra of pure water evidence the angular jumps during water reorientation?

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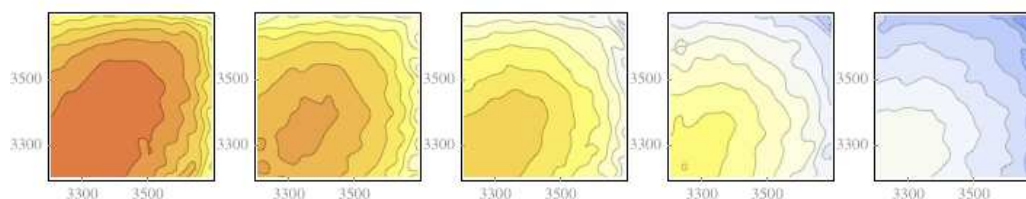
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At ambient temperature, liquid water forms very dynamic, labile hydrogen (H)-bond networks. A major fashion in which this network constantly rearranges by breaking and forming H-bonds is through the reorientation of water molecules. One of us, among others, recently suggested that this reorientation proceeds mainly through large-amplitude angular jumps involving H-bond partner exchange for the reorienting water molecule.¹ The reorientation is described within an Extended-Jump-Model. This molecular jump mechanism was evidenced in MD simulations, and leads to time constants consistent with all experimental data e.g. from NMR, ultrafast IR and neutron scattering. However, these jumps have never been directly evidenced in experiments yet.

We investigate here whether a recent spectroscopy technique, two-dimensional vibrational spectroscopy (2D-IR)² could evidence these jumps. We computed the first 2D-IR anisotropy spectra, the two-dimensional analogs of the one-dimensional anisotropy measured with pump-probe ultrafast IR. As the frequency of the OH stretch is a very sensitive probe of its environment, this technique provides insight on which configurations reorient faster.

We show that 2D-IR anisotropy exhibits a clear frequency dependence beyond the fast initial librational decay. By interpreting the 2D-IR anisotropy in terms of frequency-resolved orientational time correlation functions, we show that its frequency dependence can be connected to the mean number of jumps experienced by an OH for given initial and final frequencies, and develop a frequency-dependent version of the Extended-Jump-Model.¹ We therefore suggest that 2D-IR anisotropy measurements³ should provide a more direct observation of angular jumps in water.

T=0.1 ps T=0.2 ps T=0.5 ps T=1 ps T=2 ps



Keywords: water reorientation, 2D-IR spectroscopy, extended jump model

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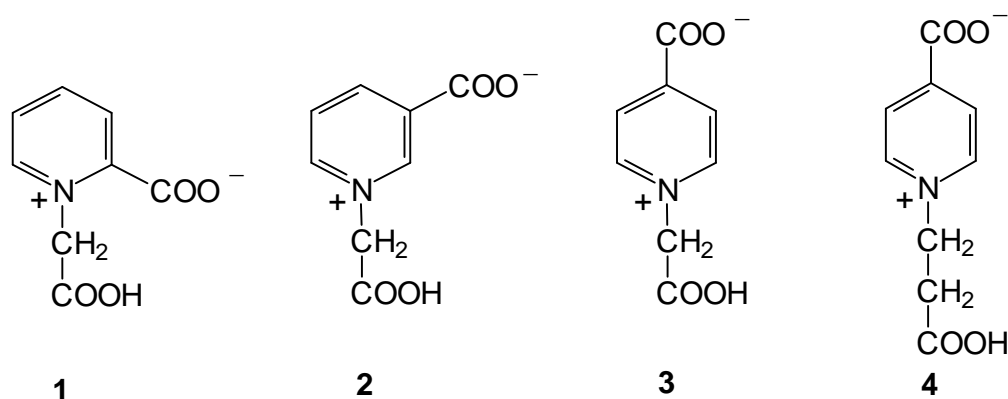
P-A 48: Hydrogen bonds in 1-carboxyalkylpyridinium-carboxylates

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Betaines [$\geq N^+(CH_2)_nCOO^-$] are zwitterions (inner salts) containing quaternary ammonium or pyridinium moiety and carboxylate group separated by CH_2 groups. Pyridine carboxylic acids (picolinic, nicotinic and isonicotinic) upon methylation are converted into other betaines (inner salts): homarine (1-methylpyridinium-2-carboxylate), trigonelline (1-methylpyridinium-3-carboxylate) and 1-methylpyridinium-4-carboxylate and their structures have been determined by X-ray diffraction. Other interesting molecules are 1-carboxymethylpyridinium-2-carboxylate, **1** [1], 1-carboxymethylpyridinium-3-carboxylate, **2** [2,3] and 1-carboxymethylpyridinium-4-carboxylate, **3** [4] inner salts, which are dicarboxylic betaines.



In this work we analyze crystal structures, spectral data, H-bonds and electrostatic interactions of the 1-carboxymethylpyridinium-4-carboxylate (**3**) and 1-carboxyethylpyridinium-4-carboxylate (**4**) inner salts. Each molecule of 1-carboxymethylpyridinium-4-carboxylate inner salt (**3**) is engaged in two short and asymmetric O-H \cdots O hydrogen bonds of the lengths 2.449(2) and 2.481(2) Å with two adjacent molecules through head to head and tail to tail connections. In 1-carboxyethylpyridinium-4-carboxylate inner salt (**4**) the connection between adjacent molecules is different. The acidic proton residing on the carboxyethyl group forms a strong and asymmetric O-H \cdots O hydrogen bond of the length 2.533(2) Å with the ring carboxylate group of an adjacent molecule (head to tail).

The FTIR spectra of both investigated inner salts show a broad and intense absorption in the 1600-900 cm^{-1} region, typical of such short hydrogen bonds. Linear correlations between the experimental ^{13}C and 1H NMR chemical shifts (δ_{exp}) in D_2O and the GIAO/B3LYP calculated isotropic shielding tensors (σ_{cal}), $\delta_{exp} = a + b \sigma_{cal}$, are analyzed.

Keywords: X-ray structures, DFT Calculations, H-bonds, electrostatic interactions

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P-A 49: Low-Temperature NMR Spectra of a System of Hydrogen Bonds Modeling the Catalytic Centre of Serine Proteases

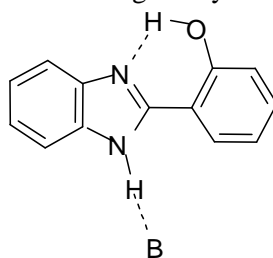
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¹H, ¹⁵N and ¹³C NMR spectra of partially deuterated in mobile (OH and NH) sites complexes of o-hydroxyphenyl-benzimidazol-¹⁵N₂ (HPBIm) with a number of proton acceptors, B, of rising basicity were recorded at 110 – 300 K in CD₂Cl₂ and the mixture, CDF₃/CDF₂Cl, as solvents. The complexes of HPBIm with anionic oxygen bases, B = RCOO(-), involve a system of coupled hydrogen bonds similar to that found in catalytic sites of serine proteases and called as charge relay chain.



The analysis of the spectra permitted to establish NMR values for four isotopic forms in equilibrium, namely, HH, two non-equivalent HD and DD. Thus measured long-range isotope effects allowed us to evaluate the dynamic coupling of O-H and N-H covalent bonds separated by imidazole ring and one hydrogen bond. The off-diagonal harmonic force constant rises with hydrogen bond strengthening and, probably, originates itself from mutual polarization of two coupled hydrogen bonds. The estimated values proved, however, to be considerably higher than those calculated *ab initio* (MP2/6-31G (p,d)). It can be assumed that the polar solvent (CD₂Cl₂) takes an important part in hydrogen bond polarization.

Within the limit of experimental error, the measured values of scalar spin couplings, ¹J_{NH}, do not depend on temperature. This indicates the absence of fast double proton transfer, OH...N(Im)NH...O(-) = O(-)...HN(Im)N...HO, which was assumed in several papers as a mechanism of charge transfer across a system of hydrogen bonds. Nevertheless, the proton and nitrogen chemical shifts exhibit exceptionally strong temperature dependence. This can be rationalized in terms of the OH...N intramolecular H-bond to get stronger with shortening the intermolecular NH...O(-) one due to their mutual polarization, or extremely strong co-operativity. The results obtained are in favor of a mechanism of charge relay in the hydrogen bonded system without the real transfer of protons.

Keywords: NMR, Coupled H-Bonds, Charge Relay Chain, Serine Protease

P-A 50: Proton Transfer of 4-Methyl-1H-Pyrazole Induced by Mesoporous Silica Surfaces

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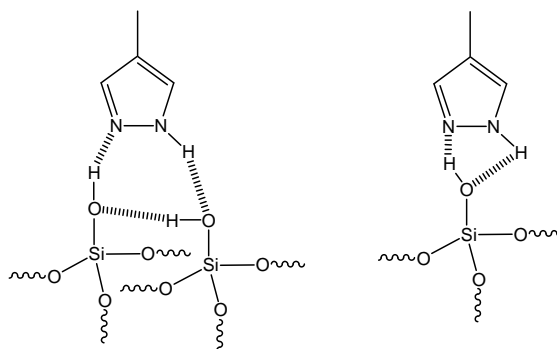
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Micelle-templated silica materials are characterized by a well-defined porosity, although the silica matrix is disordered in an atomic length scale [1-3]. To improve our knowledge on the structure of the inner pore surface and its ability to catalyze proton transfer reactions, we have performed ¹⁵N and ¹H solid state NMR experiments on 4-methyl-1H-pyrazole at different loadings in MCM-41 and SBA-15 samples. Low temperature ¹⁵N CPMAS experiments of bulk 4-methyl-1H-pyrazole showed a slow intermolecular proton transfer in the NMR time scale. In contrast, when the pyrazole was loaded in MCM-41 at submonolayer coverage, at least two different environments with different proton transfer rates and slow site-exchange were observed. The fast regime for proton transfer, site-exchange, rotational diffusion and translational diffusion was reached at 125 °C. High temperature one pulse ¹H spectra recorded for samples with increasing loadings allowed us to estimate the number of surface silanol groups and model possible host-guest complexes.



Keywords: proton transfer, silica, pyrazole, NMR

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P-A 51: DFT study of H-bonds in the peptide secondary structures. Side-chain-backbone interactions and salt bridges

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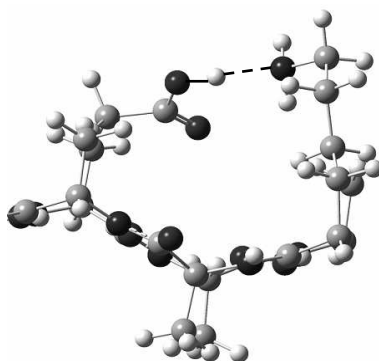
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Very recently we developed approach [1] which is based on the combined use of the DFT methods with/without periodic boundary conditions and the simultaneous consideration of the frequency shifts of the H-bonded groups and electron-density properties of the non-covalent interactions. The effects of complexity, e.g. introduction of large residues or solvent effects can be studied step by step in this treatment. It was used for the quantitative description of the H-bonds defining the intrinsic local conformational preferences of the alanine-based secondary structures. The size of the species goes up to 11 residues and all types of the secondary structures, including the protein α -helixes were studied at the same computational level. According to [1], the energies of the primary N–H...O H-bonds are decreasing in the following way: C13 > C5 \geq C7 > C10. The energies of the secondary N–H...O, N–H...N and H...H interactions are comparable to those of the primary H-bonds (~ 4.5 kcal/mol).

This approach is applied to study the side-chain–backbone and backbone–backbone interactions in the infinite models of the alanine-based two-stranded β -sheets modified by the glycine and lysine/glycine residues, respectively. Several low-energy structures are localized by the BLYP/plane-wave computations. The minimum-energy equilibrium states of the structures are confirmed by calculating the harmonic frequencies.

The strongest side-chain–backbone interaction (~ 11 kcal/mol) is due to the H-bond formation between the COH side-chain group and the O=C backbone group. Computed H...O=C distance equals to 1.727 Å. The frequency shift of the stretching vibration of the considered OH group, $\Delta\nu(\text{OH})$, is around 370 cm^{-1} .

The backbone–backbone interaction occurs between the glycine COH group and lysine NH₂ group, see Figure. The bridging proton locates near oxygen, however, $R(\text{O–H}) = 1.021$ Å. The O...N distance equals to 1.770 Å and $\Delta\nu(\text{OH}) = 771$ cm^{-1} . The computed values indicate the formation of strong interchain H-bond. Inclusion of the solvent effects will shift the proton from O to N, i.e. will lead to the formation of the so-called salt-bridges.



Keywords: DFT periodic boundary conditions, H-bonds, peptide secondary structures

[1] M.V. Vener, A.N. Egorova, D.P. Fomin and V.G. Tsirelson, *J Phys. Org. Chem.*, **22** 177 (2009).

P-A 52: Raman spectra of carboxylic acid dimers

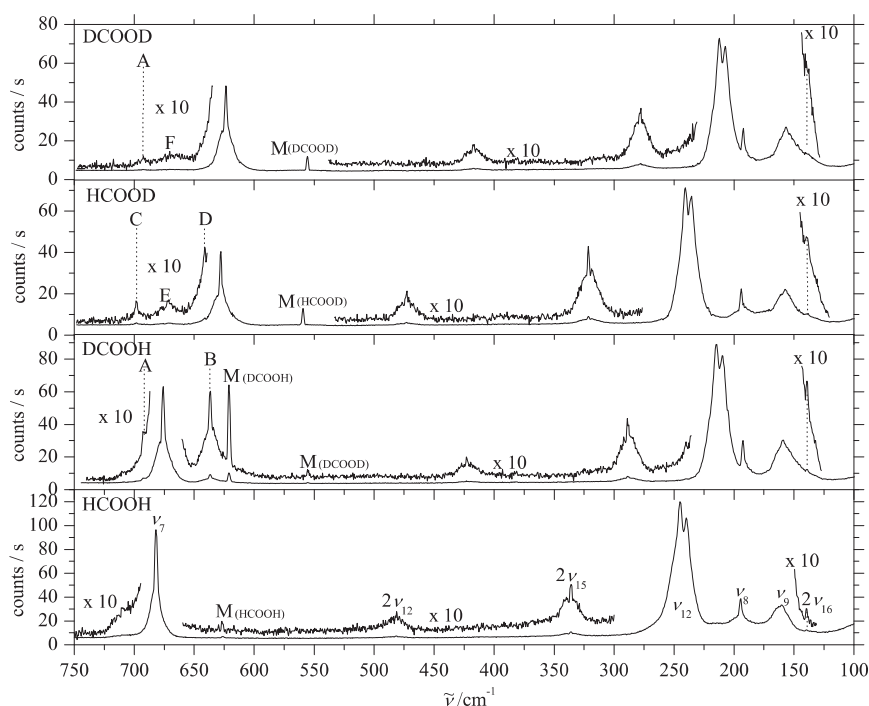
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Proton transfer in hydrogen-bonded systems is among the most fundamental processes in biology and chemistry. The sensitivity of this quantum dynamical process to structural details is very large. The centrosymmetric carboxylic acid dimers serve as prototype cyclic complexes involving two equivalent hydrogen bonds and are very common in crystal structures of organic compounds. Therefore, as the two smallest carboxylic acids, formic acid and acetic acid have been subject to intense experimental and theoretical investigations [1-3].

Under jet-cooled, vacuum-isolated conditions we have recorded all their Raman active fundamentals in the fundamental wave number range ($100\text{-}3600\text{ cm}^{-1}$) as well as overtones and combination bands of formic acid dimer in the intermolecular region ($100\text{-}700\text{ cm}^{-1}$), and assigned them with the help of isotope substitution. Individual anharmonicity effects are shown to be small, where they are accessible by experiment. However, they may accumulate to substantial differences between harmonic and anharmonic fundamental excitations. Preliminary jet experimental evidence for the most elusive fundamental vibration of formic acid dimer, symmetric OH torsion, is presented. A rigorous experimental reference frame for existing and future high level quantum chemical and dynamical treatments of this important prototype system is provided.



Keywords: carboxylic acid dimer, overtone/combination band, anharmonicity

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P-A 53: Peculiarities of H-complexes formations in behenic acid: FTIR-spectra and structural-dynamical models

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Long-chain aliphatic compounds are characterized by conformational polymorphism and the orientationally disordered motions of different types, performed by their molecules even in the temperature range below the melting point. The mechanisms of their structure formation and phase transitions are a subject of scientific interest due to their complex nature and practical importance.

The FTIR absorption spectra of the behenic acid, CH₃(CH₂)₂₀COOH, kC₂₂, have been measured in a wide temperature range of 11 – 363 K (up to above the melting) and analyzed. The molecules of this compound are known to form H-bonded complexes, mostly consisting of dimer structures. These dimers are connected by C=O...H-O hydrogen bonds and differ from each other by the orientations of a carboxylic group relatively to an alkyl chain, and the location of a molecule fragment, including a carboxylic group and the closest CH₂-group regarding the rest of the alkyl chain.

At heating, the strength of the H-bonding becomes less, and the conformation of the H-complexes is changed. These conclusions are made from the temperature dependencies of the kC₂₂ experimental data, recorded in the spectral ranges of the C=O (1660-1760 cm⁻¹) and C-O (1160-1290 cm⁻¹) stretching vibrations, and also of the O-H stretching (2400-3500 cm⁻¹) and out-of-plane deformation (950-1000 cm⁻¹) vibrations.

To confirm the assumptions made about the conformational mobility of the behenic acid H-complexes with temperature, the theoretical modeling of the different kC₂₂ dimer structures and calculations of their IR spectral peculiarities were carried out. The DFT (B3LYP/6-31G(d)) method was used; and the energy minimization, structure optimization and the calculations of the electro-optical parameters were made. The harmonic force fields, IR harmonic frequencies and intensities were determined for different conformers, formed by the kC₂₂ dimers.

Based on the calculated theoretical results, the explanations of the temperature changes in the IR spectra of the kC₂₂ are given. The H-bonding energy value is estimated; and the conclusions about the conformational mobility of the kC₂₂ molecules in the different phases and the heterogeneity of the conformational composition of the sample are presented.

Keywords: behenic acid, IR-spectra, conformations

P-A 54: Molecular complexes: H-bonding and charge transfer

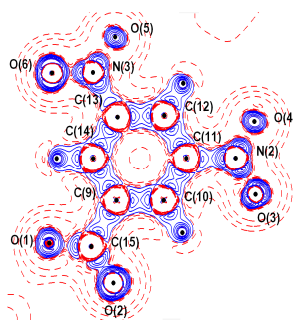
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The current work is devoted to the investigation of the interplay of ionic hydrogen bond strength and charge transfer in molecular complexes [1] of pyridine and piperidine with carboxylic acids via the topological analysis of charge density distribution function ($\rho(r)$) [2] reconstructed from the X-ray diffraction data.

Despite the fact that the charge redistribution due to the H-bond formation is well-known [3] the investigations were mainly concentrated on the hydrogen charge variation rather than on the charges of donor and acceptor atoms. Analyzing the experimental values of atomic charges and volumes in the crystals of piperidinium succinate, piperidinium adipate, piperidinium tartrate monohydrate as well as piperidinium 2,4-dinitrobenzoate and 3-nitro-4-chlorobenzoate we investigated the manifestation of H-bonding in the charge variation of anion/cation.



It was shown that the higher hydrogen bond energy corresponds to the higher charge transfer between anion and cation moieties as well as to the increase in charge of hydrogen atom.

Authors are grateful for financial support RFBR 08-03-90103-mol.

Keywords: molecular complexes, charge transfer, high-resolution XRD

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P-A 55: Theoretical study of hydrogen bond between substituted phenol – substituted pyridine in aprotic solvents

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In our study we use theoretical computations to find out quantum chemical approaches suitable to describe correctly properties of strong intermolecular hydrogen bonds in gas phase and condensed matter. The key point of our study is to inspect systems those geometries are known from experiments. We focus on the systems with strong intermolecular H-bond, in which the proton transfer can occur, e.g. substituted pyridine - substituted phenol complexes (*pp* complexes). In the gas-phase of pyridine-phenol complexes the potential of the O-H...N fragment has only one well and the bridging proton usually locates near the oxygen atom. Most of the experimental studies of the *pp* complexes done in condensed phase, i.e. polar solvents^[1] or molecular crystals^[2]. According to these studies, proton transfer does occur in these systems. That is an increase of solvent polarity shifts the bridging proton from the oxygen to the nitrogen atom of the hydrogen bonded fragment. To bridge a gap between gas-phase computations and condensed-phase experimental investigations of the strong intermolecular hydrogen bonded complexes with the O-H...N fragment, DFT calculations have been started. We check the applicability of different DFT functionals in gas-phase for description of a proton-transfer system. An analysis of some *pp* complexes let us to conclude that the PBE functional is a suitable functional for calculating the proton-transfer complexes. Also we find out that strong electron acceptors on the meta- and ortho position of the phenol ring prompt the protontransfer. After that we study how the dielectric constant of polar solvents influences the geometry of O-H...N hydrogen bonds. As model we choose 4-amino-pyridine-2,3,5,6-tetrachloro-4-nitrophenol, because it has strong hydrogen bond in the gas-phase calculation. Proton transfer does occur in aprotic solvents. In the solvents with small value of dielectric permittivity () the bridging proton locates near to the oxygen atom. By increase of the bridging proton shifts tendentially to the hydrogen bond center and locates somewhere between the O and N atoms. In solvents with $\epsilon \geq 2$ the bridging proton locates near the N atom. And the position of the bridging atom is extremely sensitive to the distance between two heavy atoms. When $R(O...N) \approx 2.45 \text{ \AA}$ the bridging proton transfer occurs. When $R(O...N) \geq 2.45$ the bridging proton locates prefer to the heavy atom.

Keywords: hydrogen bond, pyridine - phenol, aprotic solvent, dielectric permittivity

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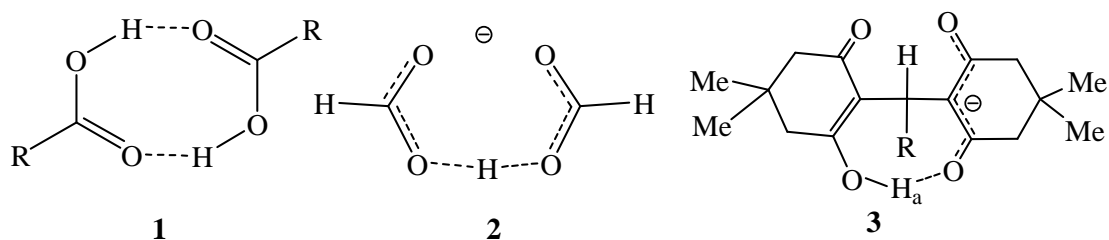
P-A 56: Strong intramolecular hydrogen bonding in dimedone-aldehyde adducts

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The hydrogen bond strength in the carboxylic acid dimers (**1**) was estimated to reach 7 kcal/mol per bond. This bond is classified as moderate. Ionization of one acid molecule of the dimer gives rise to formation of the carboxylate – carboxylic acid system involving the anionic hydrogen bond. Ionic hydrogen bonds were observed experimentally and intensively studied theoretically [1]. Experimentally, these strong hydrogen bonds are characterized by the low-field ^1H NMR chemical shift (16 – 22 ppm) of the bonded proton [2]. Quantum mechanical calculations for the simplest pair formic acid – formate anion (**2**) yielded 22 – 27 kcal/mol depending on the level of theory [3]. However, experimental spectroscopic evaluation of the ionic hydrogen bond strength in solution was not attempted to the best of our knowledge.



The results of our investigation on the ionic hydrogen bonding in dimedone derivatives will be presented. Ionization of the well-known 2:1 dimedone-aldehyde adducts, featuring two hydrogen bonds per molecule, leads to the corresponding monoanions **3**, involving the ionic hydrogen bond. The monoanions are characterized by the short $\text{O}\cdots\text{H}_a\cdots\text{O}$ distance in solid state (2.40 Å for $\text{R} = p\text{-ClC}_6\text{H}_4$), equalization of the corresponding bond lengths in the vicinity of the hydrogen bonded moieties, and a strong downfield shift of the acidic proton signals in solution ($\delta\text{H}_a = 17.0$ ppm, in dichloromethane- d_2). The negative charge is delocalized over the both *non-conjugated* dimedone moieties. These features are also reproduced by the quantum mechanical calculations. The barrier to internal rotation obtained by dynamic NMR analysis provides an estimate of 8.3 kcal/mol per bond for the hydrogen bonds in the neutral adduct and 16 kcal/mol for the ionic hydrogen bond in the anion **3**.

Keywords: strong hydrogen bonds, dynamic NMR, DFT calculations

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P-A 57: Isolated H-bonds of Phenols Studied by UVNMR: Spectroscopic Correlations, Proton Tautomerism, and Solvent Effects

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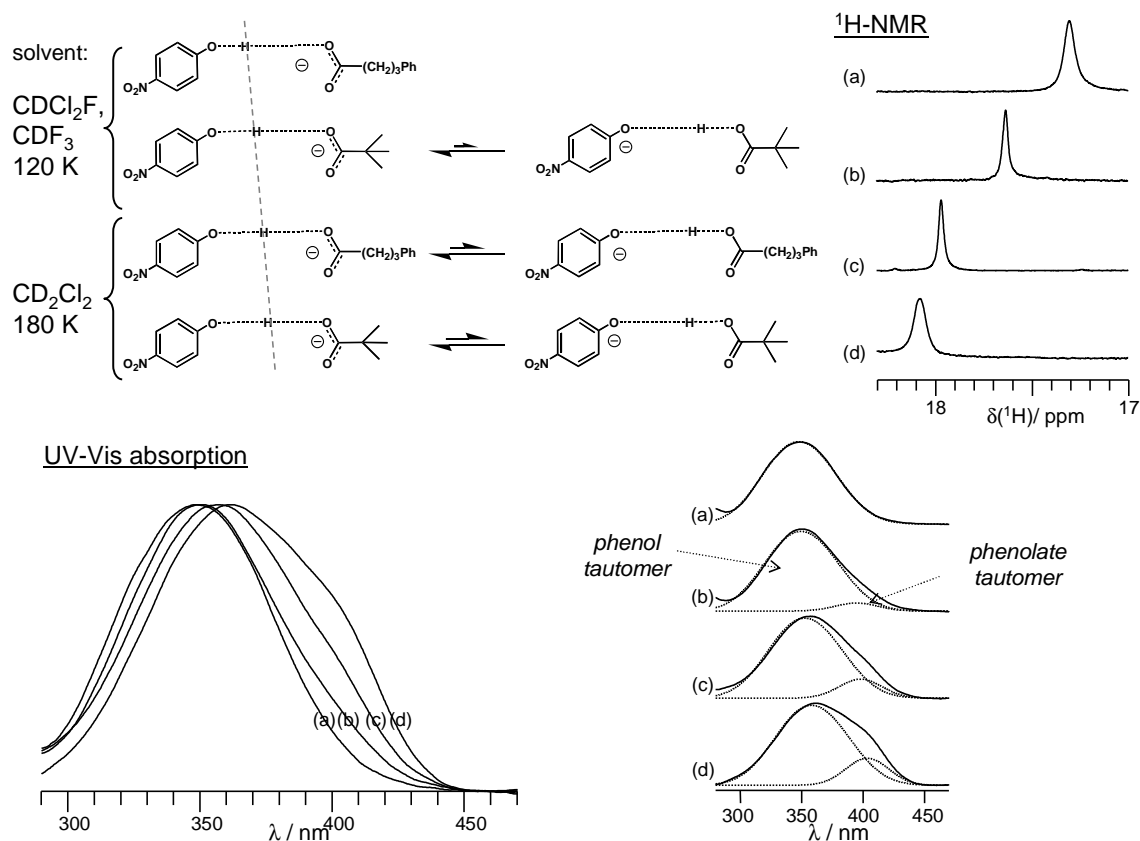
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UVNMR [1] is a technique for the simultaneous measurement of NMR and UV-Vis absorption spectra. It combines the high content of structural information of NMR spectra with the superior time resolution of optical spectra. It may thus provide valuable information on H-bonded structures exhibiting dynamics fast on the NMR timescale.

The method allowed us to correlate UV-Vis absorption band shifts of phenols in strong hydrogen bonds with the corresponding H-bond geometries as determined by NMR. In turn, the optical spectra enable us to detect short lived species such as tautomeric forms of a H-bond and to estimate the geometries as well as the population ratio of these tautomers.

Systems studied include charged OHO (see figure) and uncharged OHN H-bonds of phenols with carboxylic acids and pyridines, respectively. Particular focus lies on the effects of temperature and the polarity of the aprotic solvents CD_2Cl_2 and CDCl_2F / CDF_3 on H-bond geometry: in both classes of complexes discussed, medium effects may lead to shifts of the average proton position through the center of the hydrogen bond.



Keywords: UVNMR, H-Bond Correlations, Proton Tautomerism, Solvent Effects

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P-A 58: Rotational spectroscopy of molecular complex of alcohols and ethers: Ubbelohde effect and transient/permanent chirality

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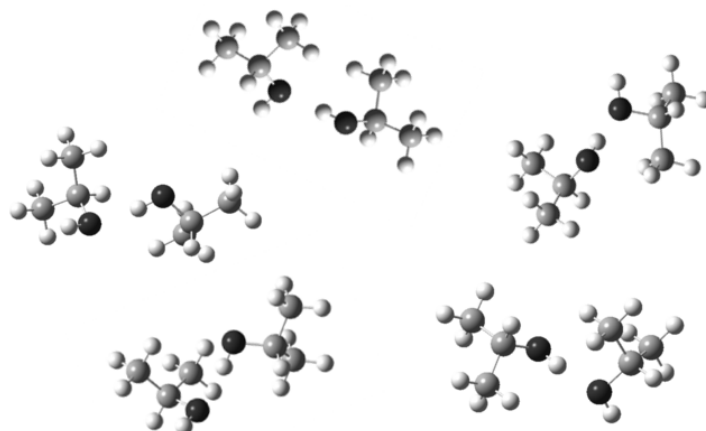
Hydrogen bonding plays an important role in determining the energetic and structural aspects of chemical and biological system.

Here we report the results of a Fourier Transform Microwave Spectroscopy (FTMW) study, assisted by high level *ab initio* calculations, of some molecular adducts, namely: *tert*-butanol - (CH₃)₂O, isopropanol - (CH₃)₂O and isopropanol dimer. From these investigations we observed some interesting features related to the involved Hbonds.

a) Sizing of the Ubbelohde effect [1]. In *tert*-butanol - (CH₃)₂O, when going from the OH to the OD species, the *B* and *C* rotational constants increase, due to shrinking of the O...O distance.

b) Inertial effects change transient to permanent chirality. The two mirror images of *gauche* isopropanol are connected through the low energy barrier of the OH torsion potential energy surface. This produces large tunnelling splittings in the rotational spectrum [2,3]. Upon formation of the isopropanol - (CH₃)₂O complex, the inertial effects quench the tunneling and, in the time scale of MW spectroscopy, such a system appears as made of a pair of "classical" enantiomers.

c) Molecular recognition and induced chirality. We could assign the rotational spectra of five chiral dimers of isopropanol (see Figure below), deriving either from the combinations of different conformers or from the different chiral species of this alcohol, whose chirality is "permanent" in the dimers.



Keywords: rotational spectroscopy, hydrogen bonds, isotope effects, supersonic expansions, molecular complexes

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P-A 59: Hydrogen bonding, proton transfer and conformational changes in bifunctional heteroazaaromatics

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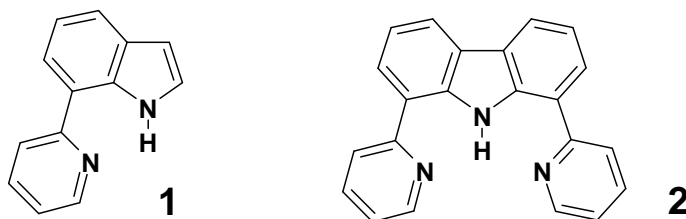
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Bifunctional azaaromatic compounds, possessing both hydrogen bond donor and acceptor moieties reveal rich and complicated photophysical behaviour, depending on the environment.¹ The molecules with the donor and acceptor groups appropriately positioned with respect to each other can undergo excited state proton transfer along the intramolecular hydrogen bond accompanied by twisting of the donor and the acceptor units.² The time scales for the proton transfer and twisting, as well as height of the barrier for the radiationless deactivation in the phototautomeric form, can be controlled by changing the strength of the intramolecular hydrogen bond. This will be illustrated by the results obtained for two similar compounds, 7-(2'-pyridyl)indole (**1**) and 2,9-(di-2'-pyridyl)carbazole (**2**).



Two isomers of **1**, 7-(3'-pyridyl)indole (**3**) and 7-(4'-pyridyl)indole (**4**) can form intermolecular hydrogen bonds with water or alcohols. Various geometries of singly and doubly complexed molecules are possible, including cycling and noncyclic binding modes. The experimentally determined structures of such complexes will be presented, along with the structure-photophysics relationships.



Keywords: excited state proton transfer, radiationless transitions, fluorescence quenching

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P-A 61: Structure analysis of hydrogen-ordered ice XI using neutron powder diffraction and infrared spectroscopy

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Recently, existence of naturally occurring ice XI in space was proposed [1]. The existence of ice XI in our solar system and Galaxy may affect the formation mechanism of icy planets because of its long-range electrostatic forces caused by its ferroelectricity [1,2,3]. Ice XI has been prepared so far only from KOD-doped aqueous solutions, and the influence of the dopant on longrange ordering was not well resolved. By ionization of potassium hydroxide, the OH⁻ ions replace H₂O sites in the ice, and the replaced ions presumably increase the mobility of the protons, and accelerate the phase transition within the time of an experiment. In order to discuss the existence of the ferroelectric ice XI in the Universe, we need to confirm that the hydrogen ordering occurs independent of the cations from the dopants. We prepared ice XI from different kinds of alkali metal hydroxide solutions, and measured neutron powder diffraction at JRR-3 (Japan Atomic Energy Agency, Japan). The measurements were performed at 10 K, and the diffraction patterns were collected in the range of $2\theta = 2.50\text{--}162.45^\circ$ using a wavelength of 1.82035 Å. Rietveld analysis was carried out on the structural parameters for a two-phase model, which includes ice Ih and XI. The hydrogen-ordered structure in lithium-doped ice was exactly same as that in the sodium-doped ice. Furthermore, we obtained a scattering amplitude density distribution using a maximum entropy method in order to understand vibrational amplitude of hydrogen in the ferroelectric ice. The analysis shows that the amplitude of hydrogen is larger on hydrogen bonds parallel to c axis. The obtained results suggest that the ferroelectric ordered-structure is a stable and intrinsic form of the low-temperature phase of ice Ih.

Furthermore, we measured IR spectra of KOH-doped film ice to investigate spectral changes caused by hydrogen ordering. In the near future, infrared (IR) spectra of icy planets of our solar system will be obtained by IR telescopes and planetary explorations. Infrared observations of icy planets and our results will reveal whether ferroelectric hydrogen-ordered ice exists in the universe.

Keywords: water, ice, infrared spectroscopy, neutron

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IV.B. Section B

P-B 1: NMR Studies of acid-base interactions, hydration and secondary structures of Poly-L-lysine

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The interaction of dry solid poly-L-lysine (PLL, Figure 1) with acids has been studied using ¹⁵N solid state NMR. Assisted by *ab initio* calculations it is shown [1] that oxygen acids and HF form hydrogen bonded complexes (C) of different strength in both the β -pleated sheet and the α -helical structures. By contrast, HCl, HBr and HI can also form salt structures S. For that α -helical regions have first to be converted into β -sheets. When the number R of interacting acid molecules per residue is reduced, homoconjugate complexes are formed involving 2 or 3 amino groups per acid molecule [2]. A further reduction of R leads to a superposition of domains with free bases and with homoconjugate cations in different domains. Hydration experiments [3] show that several water molecules per residue are necessary for interconversion of these domains to occur in the NMR time scale. However, proton transfer within the acid containing domain is induced already by less than 1 water molecule. In the case of salt structures water molecules are inserted in the NHX hydrogen bonds of the and hydration leads to a change from β -sheets to α -helical regions.

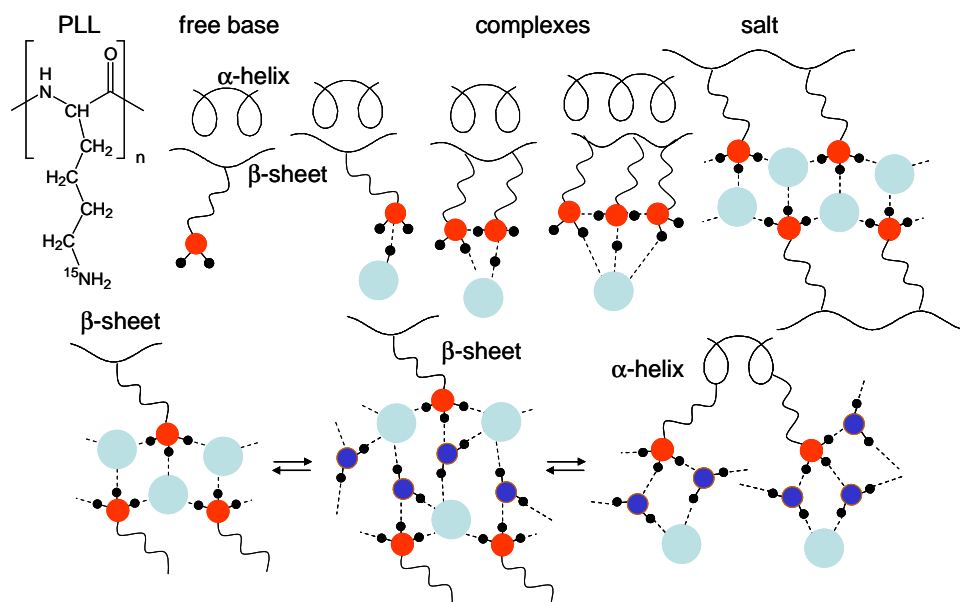


Figure 1. Acid base interactions and hydration of poly-L-lysine (PLL)

Keywords: Poly-L-lysine, Solid State NMR, Acid-Base Interactions, Hydrogen Bonding, Hydration

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P-B 2: Hydrogen bond networks in trehalose water solutions: a neutron diffraction experiment.

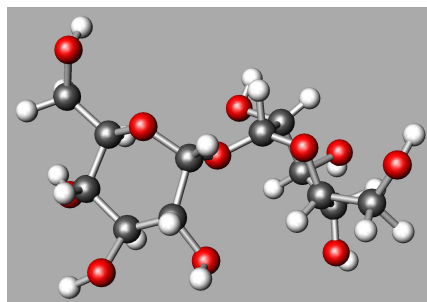
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Trehalose is a disaccharide, like maltose and sucrose, produced by a few varieties of plant seeds, spores, cysts of certain crustaceans, and some species of soil-dwelling animals as they pass, in dry times, into a state of suspended animation, usually referred to as *anhydrobiosis*. The ability of these organisms to survive to drought and revive upon rehydration after periods as long as 120 years [1,2] is ascribed to the peculiar properties of trehalose compared to other disaccharides, in spite of the similar chemical composition. It has been suggested that the key for understanding the role of trehalose as stabilizer and protective agent against environmental stresses of biomolecules can be found in its interaction with water molecules in cells and several hypotheses and models have been proposed [3]. Here we report the results of a neutron diffraction experiment, performed on two water-trehalose solutions (namely 1 solute per 100 water molecules and 1 solute per 25 water molecules), aimed at investigating the presence of water-trehalose HB along with the influence of this disaccharide on the HB network of water. The relevant distribution functions extracted from the data demonstrate that, although the number of water molecules in the first neighbor's shell of trehalose is relevant, only a few of them are hydrogen bonded, and that the microscopic structure of water is barely distorted by the presence of this solute.



Keywords: trehalose, water, hydrogen bond

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P-B 3: A Quantum Reaction Dynamics Study of Double Proton Transfer in the Model System Porphine

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Double Proton Transfer (DPT) was a widely studied topic in the last decades. Porphyrins and metalloporphyrins are one of the most common subjects of research. These "pigments of life" play a crucial role in biologically relevant processes, such as photosynthesis, oxygen transport and activations and therefore they drove to the development of theoretical models for systematic studies. Questions of interest in this field concern the nature of the DPT: concerted (called 1-step or synchronous, as well) or sequential (called 2-step or asynchronous, as well) reaction mechanism [1,2,3], influences of quantum effects on reaction rates, and possibility to control the DPT are just few examples [4].

We present a quantum-mechanical reaction dynamics approach to DPT in porphine, using the symmetric model of Smedarchina et al. [5]. Such approach has the advantage to give information about the quantum dynamics of the wave packets far away from the minimum energy path in a multidimensional space.

In order to carry out the quantum dynamics, the MCTDH method [6] was applied. The propagated nuclear wavefunctions discover a surprising phenomenon in DPT, i.e. the mechanism may switch from concerted to sequential. We conclude that, in general, it is not sufficient to consider just the potential energy surface (PES) in order to predict the mechanism of DPT. The same PES may support different reaction mechanisms depending on the initial preparation of the system. The discrimination of the mechanism calls for quantum dynamics simulations, beyond quantum chemistry calculations of the PES.

Keywords: Porphine, Double Proton Transfer, Quantum Reaction Dynamics.

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P-B 4: Investigation of the active site models of carbonic anhydrase by low temperature liquid state NMR spectroscopy.

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Hydrogen transfer plays an important role in biological catalysis. In reactions catalysing enzyme, a huge complex structure is involved in transferring of hydrogen atoms into the right place at the right time so that the reaction can be catalytically enhanced, with rates orders of magnitude larger than those in solution.

The experimental investigation of such huge systems connects often with difficulties in sample preparation or data interpretation. One of the approaches involves the study of prototypical but well-defined molecular systems.

The striking examples are the model compounds developed by Vahrenkamp and other which mimic the active site of carbonic anhydrase. Carbonic anhydrase is a widely occurring Zn^{2+} metalloenzyme. The essential physiological function of the enzyme is to catalyze the reversible hydration of carbon dioxide $CO_2 + H_2O = HCO_3^- + H^+$ with a turnover rate of about 10^6 reactions per second. Carbonic anhydrase is one of the best investigated enzymes. The investigations of the enzyme and its models have been carried out using different theoretical and experimental methods. However, the applied methods, for instance X-ray or IR spectroscopy, could give in that particular case just approximate information about the structure of intermediate or even starting complexes. In contrast, the NMR spectroscopy allows to observe directly the processes occurring on protons or heteroatoms as ^{13}C and ^{15}N .

In the present work we show the new approach to investigate the complexes by low temperature NMR spectroscopy in aprotic solvents as CD_2Cl_2 or Freon mixture. The NMR spectroscopy gives us an opportunity to follow results obtained by other methods to get additional information and cover the gaps in knowledge about such important properties of Zn-OH group as pK_a value, its role in interactions with CO_2 and N - bases.

IV.C. Section C

P-C 1: Display of Resonance Intermolecular Interaction in IR Spectra for Crystalline Carboxylic Acids at Phase Transitions

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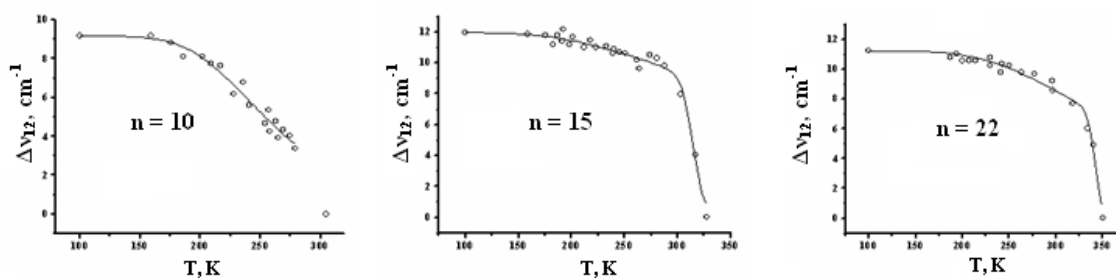
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In the present paper we report on temperature dependent FTIR spectra studies of Davydov splitting value ($\Delta\nu_{12}$) for the in-phase CH_2 rocking vibrations of methylene chains in crystalline n-carboxylic acids $\text{CH}_3(\text{CH}_2)_{n-2}\text{COOH}$ with odd ($n = 15, 17, 19$) and even ($n = 10, 14, 16, 22$) numbers n of carbon atoms in the temperature region from $T = 100$ K to the crystal melting point.

The analysis of obtained temperature dependencies allows to determine the following regularities. For all acids in the region of low temperatures the Davydov splitting value practically does not depend on temperature. When temperature increases for acids with odd number $n=10, 14, 16$ of carbon atoms the splitting value decreases to zero without sharp changes. For acids with odd number and even number $n=22$ of carbon atoms, the slow decreasing of the splitting value and then sharp decreasing to zero in the nearest region to the crystal melting point takes place.

A statistic-dynamic model is proposed which provides an adequate description of the observed effects. In the frameworks of this model two different mechanisms are responsible for the temperature changes of the vibrational modes splitting value. In addition to the thermal expansion of crystals at heating, the damping of vibrational excitons on orientational defects of different nature takes place. Genesis of such defects is related to the excitation of conformational, librational and rotational degrees of freedom of H-bonded molecular dimers at different temperatures.

Theoretical analysis of resonance dynamical intermolecular interaction effect on the intramolecular vibrations spectra of the crystals was performed in the terms of stochastic equations with account of such mechanisms. The explicit expression for the theoretical dependence of Davydov splitting value on temperature was obtained. Computer simulation of such dependence was performed for crystalline normal chain carboxylic acids. Good agreement between the experimental data (dots) and computer simulation results (lines) takes place.



Keywords: Carboxylic acid crystals; Davydov splitting; Damping of vibrational excitons; Conformational transitions; Librations; Rotations; IR spectra.

P-C 2: Ferroelectric properties of squaric acid: quantum-chemical modeling of structural phase transition.

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The H/D bonded crystals of squaric acids $\text{H}_2\text{C}_4\text{O}_4$ (H_2SQ) and $\text{D}_2\text{C}_4\text{O}_4$ [1] are investigated in frames of the developed approach [2] based on the application of quantum-chemical models and computational schemes to the microscopic theory of order-disorder ferroelectrics. The pseudospin Hamiltonian [3] parameters - Ω (tunneling integral) and J_{ij} (Ising parameters) - for both materials were calculated in cluster approximation for several types of model clusters, that simulate the character fragments of $(\text{H/D})_2\text{SQ}$ crystal structure. The protons/deuterons transfer barriers (need to obtain the Ω integrals) and the J_{ij} parameters were obtained on different computational levels. The Hartree-Fock (RHF), density functional method (DFT/B3LYP) and many-particle perturbation theory (MP2-MP4) with several AO basis sets of 6-31G-kind (up to 6-311++G(2d,2p)) are applied. The obtained Ω and J_{ij} values were used in the frames of the molecular field approach to handle single-layer and double-layer $(\text{H/D})_2\text{SQ}$ models. According to our calculations (in spite of the technique used) the structural phase transition in the single-layer model is of the 2d-ferroelectric type and for double-layer model - of 3d-antiferroelectric type in full agreement with the experimental data [1]. It is found also that proton/deuteron coupling between the neighboring layers is about an order weaker than within the layer. The observed thermodynamic isotope effect ($\Delta T_c \approx 140\text{K}$) is mostly caused by the H/D geometrical isotope effect, while the difference in the tunneling parameters $\Omega(\text{H})$ and $\Omega(\text{D})$ plays a modest role.

This work is supported by the RFBR, Grant 08-03-00195.

Keywords: ferroelectric materials, structural phase transitions, quantum-chemical modeling

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P-C 3: Compressed H-bonds in solids. Pressure-dependent ferroelectric behavior of KDP/DKDP.

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It is well known that physical properties of $M(H/D)_2AO_4$ family solids ($A=P, As$) are closely related to its network of strong symmetric bonds $O-H/D...O \leftrightarrow O...H/D-O$.

Hydrostatic pressure effect on ferroelectric transition (FT) in KDP (KH_2PO_4) and DKDP (KD_2PO_4) as typical examples of these solids is considered in the frames of conventional pseudospin Hamiltonian:

$$H = -\Omega \sum_i \sigma_i^x - \frac{1}{2} \sum_{i \neq j} J_{ij} \sigma_i^z \sigma_j^z. \text{ Here } \sigma_i^x \text{ and } \sigma_i^z \text{ are the Pauli matrices, the parameters } \Omega(H/D) \text{ and}$$

$J_{ij}(H/D)$ describe the quantum motion of proton/deuteron along the H/D-bond and pair interaction between these nuclei at different bonds respectively [1]. These parameters are determined by means of the cluster non-empirical calculations (SCF, MP2-MP4, B3LYP) for the characteristic structural fragments of the compounds of interest [2]. The clusters geometry was taken from the neutron diffraction data [3], obtained for pressure values $P=0$ and $P=16,5$ kbar. The molecular field approximation (MFA) together with more refined Bethe cluster approach (BCA), that takes into account the nearest neighboring protons correlation, were applied to study the T_c of FT on the base of the calculated values of $\Omega(H/D)$ and $J_{ij}(H/D)$. In agreement with the experiments [4] for both techniques T_c decreases with the growth of P due to the proton/deuteron transfer barrier width and height reduction as well as owing to the diminution of the protons/deuterons effective interaction. According to the MP2-MP4 calculations for KDP at $P=16,5$ kbar the ratio $\Omega/J_0 \approx 5/6$ ($J_0 = \sum_j J_{ij}$) is close to the critical value $(\Omega/J_0)_c = 1$, that in MFA signifies the disappearance of the ferroelectric transition (the measured $P_c \approx 17$ kbar [4]). The BCA calculations yield in $P_c(KDP) \leq 17$ kbar for all acceptable values of Ω and J_{ij} . Analogous calculations for DKDP also evidence the decrease of T_c with pressure growth and lead to $P_c(DKDP)$ value greater than $P_c(KDP)$.

This work is supported by RFBR, Project 08-03-00195.

Keywords: H-bonded materials, KDP family, ferroelectric transitions, pressure effect

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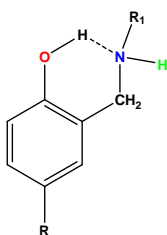
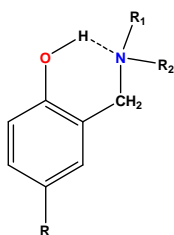
P-C 4: Competitive intra and intermolecular interactions in Mannich bases

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Intramolecular hydrogen bonds reveal enhanced structural and thermodynamic stability. Due to this they are interesting probes in the study of the nature hydrogen bonding and its dependence on surrounding and temperature. Different techniques as IR, UV-Vis and NMR spectroscopy, as well as dipole moments and average molecular weight measurements in the function of concentration were applied.



Among others, formation of dimers in Mannich bases was documented, when proton transfer reaction proceeds in weakly and medium polar solutions. In analogous systems with one N-radical substituted by hydrogen additional possibilities of aggregation appear by formation of N-H \cdots O intermolecular hydrogen bonds. Properties of such systems are discussed. Competition and mutual interactions of intramolecular and intermolecular hydrogen bonds are discussed. In crystalline state of 2-[(N-cyclohexylamino)methyl] phenol, the chains built by NH \cdots O hydrogen bonds were stated. In two nonequivalent molecules, the intramolecular O-H \cdots N hydrogen of length 2.614 and 2.601Å were found connected by NH \cdots O hydrogen bonds of length 3.07 and 3.20Å. In DFT B3LYP/6-31G(d,p) calculations it is shown that the structural parameters of both hydrogen bonds approach experimental values, when the number of interacting units becomes at least the linear trimers. The intermolecular interactions are necessary to reproduce geometry of intramolecular hydrogen bonds. In solutions in CCl₄, at concentrations lower than 0.2M no associates were stated by dipole moments and average molecular weight measurements. IR spectra show changes at higher concentrations, suggesting appearance of three different forms. The spectra in chloroform and 1,4-dioxane were applied to modulate the influence of acidic and basic centers on properties of hydrogen bonds in studied systems. UV-Vis spectra show that hydrogen bonds exist in molecular, non proton transferred tautomers.

Keywords: hydrogen bond, self aggregation, IR-spectra

P-C 5: Resonance assisted hydrogen bonding in 2-hydroxy-4-alkoxyazobenzenes

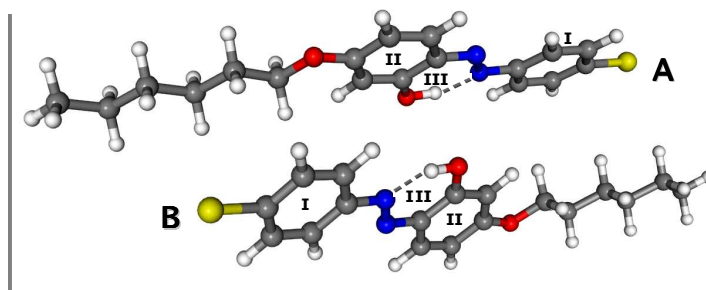
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Liquid crystalline 2-hydroxyazobenzenes are characterized by an intramolecular OH...N hydrogen bonding which shows interesting continuous absorption in infra-red spectra [i, ii, iii]. This feature is particularly well reflected in ordered phases, i.e. in the smectic and crystalline ones. In the CCl₄ solution this absorption is practically not visible that suggests a substantial influence of formation of core-to-core associates. Moreover, the behaviour of the continuous absorption depends on the length of the alkoxy chain that expresses a direct interaction of chelate hydrogen bonded rings and confirms its importance in creation of the continuous absorption.

In the present communication there is analyzed the formation of a pseudo-band at 620 cm⁻¹ due to the Fermi resonance between stretching and bending out-of-plane OH vibrations for three derivatives, namely 4'-pentyloxy, 4'-hexyloxy and 4'-heptyloxy of 4-chloro-2'-hydroxyazobenzenes. Simultaneously DFT calculations were performed for the optimized structures as shown below for the hexyloxy derivative.



These calculations clearly show an influence of the chain lengths on the conformation of associates and particularly on the mutual interaction between hydrogen bonded chelate rings.

Effect of elongation of the aliphatic chain on the Mid-Infrared (MIR) spectra for solid sample measured in function of the polarization angle is analyzed by means of the Principal Components Analysis (PCA). Both the varying orientation of these molecules due to the increase of the chain and its influence on the extend of the continuous absorption are discussed on a base of the PCA results.

Keywords: 2-hydroxyazobenzenes, resonance assisted H-bonding, influence of the core-to-core association

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P-C 6: Proton transfer in and on solids under almost water-free conditions

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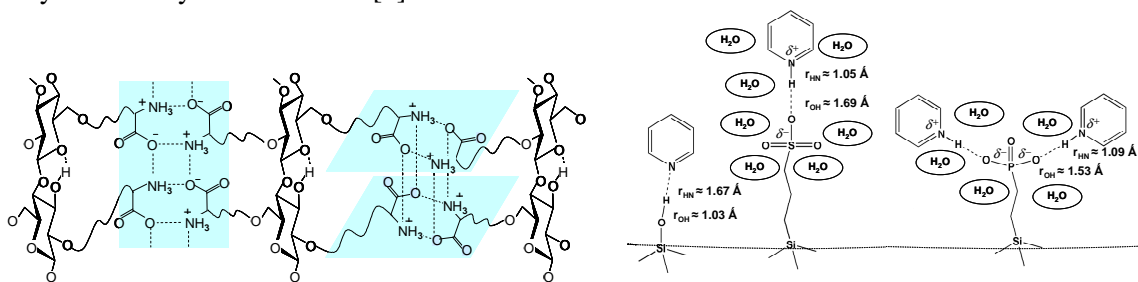
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The structure of the product of interaction between proton donor and acceptor groups depends dramatically on the environment. The general trend is well known: hydrogen bonded complexes without proton transfer, B...H-A, in the gas phase; solvent field depended geometry, B...H...A, in aprotic solutions; solvated ion pairs, [B-H]⁺ and A⁻, in aqueous solutions. The same factors, external electric fields and coupled hydrogen bonds, affect the interaction of proton donor and acceptor groups in solids. In crystals these factors can be generally controlled and the main effect can be evaluated. In contrast, for amorphous solids those are probably the most relevant materials for commercial applications, one can rarely predict neither possible hydrogen bond networks nor the presence of residual water.

In this presentation we discuss proton transfer (PT) *in* and *on* amorphous solids under almost water-free conditions. PT in solids has been studied using a cellulose based material in which L-lysine molecules are grafted with their amino side chains to the cellulose hydroxyl groups. This modification increases considerably the mechanical strength and resistance of cellulose towards water. It had been attributed to the formation of double salt bridges between lysine aminocarboxyl groups in the zwitterionic state. We have succeeded to characterize this unusual structure. It has been proved that interaction of several aminocarboxyl groups is responsible for the zwitterionic state, in contrast to the gas phase, where amino acid dimers exhibiting two OHN hydrogen bonds are neutral [1]. PT on solids has been inspected using highly ordered mesoporous silica materials. Because of their wide pore openings, narrow pore size distribution, large internal surface area, and tunable shape, ordered mesoporous silicas such as SBA-15, MCM-41, and MCM-48 have a high potential as catalytic supports and host materials for organic guest molecules and transition metals. We have shown that experimentally observing proton-donating ability of surface groups is decisively affected by residual water [2].



Keywords: proton transfer, NMR, solid state, cellulose, MCM-41, SBA-15

[1] R. Manriquez, F.A. Lopez-Dellamary, J. Frydel, T. Emmler, H. Breitzke, G. Buntkowsky, H.-H. Limbach, and I.G. Shenderovich, *J. Phys. Chem. B* **113**, 934 (2009).

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