

## I01: THE HYDROGEN BOND

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The study of the H-bond is an old topic that remains active because of its importance in science and through advances in experiment and computation [1]. The normal H-bond is generally linear and primarily electrostatic in nature. It is cooperative [2], has characteristic influences on structure and on vibrational and PMR spectra, and a binding energy  $\sim 20 \text{ kJ mol}^{-1}$ . There are other hydrogen bonds. The  $\text{FHF}^-$  anion has a dissociation energy of  $167 \text{ kJ mol}^{-1}$  and cannot be considered as an HF molecule perturbed by  $\text{F}^-$ . There are 'proton-shared' H-bonds and 'blue-shifting' H-bonds. The latter are investigated with a perturbation description of  $\text{X—H}\cdots\text{Y}$  in which the X-H bondlength change is proportional to the first derivative of the interaction energy with respect to X-H bond extension while the vibrational shift is determined by the first and second derivatives. The shift is red or blue according to the balance of these contributions.

[1] A. D. Buckingham, J. E. Del Bene and S. A. C. McDowell, *Chem. Phys. Lett.*, **2008**, *463*, 1-10.

[2] S. A. C. McDowell and A. D. Buckingham, *J. Chem. Phys.*, **2010**, *132*, 064303-(1-5).

## I02: SPECTROSCOPY OF BINARY MOLECULAR COMPLEXES

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We have measured OH-stretching and NH-stretching FTIR spectra of binary molecular hydrogen bonded complexes in the gas phase, with methanol and dimethylamine as the hydrogen donor molecules.[1] We have determined the frequencies shift and intensity enhancements upon complexation and via temperature experiments also the interaction enthalpy. The measured spectra are compared with coupled cluster ab initio calculations within an anharmonic oscillator local mode model. The ratio of calculated to measured intensity provides the room temperature equilibrium constant for formation of the binary complex governed by weak intermolecular molecular interactions. As perhaps expected no overtone transitions were observed for the complexes.[2] Measured OH-stretching overtone spectra of alkenols and alkynols and Atoms in Molecules and Non-Covalent Interactions calculations were used to analyse the weak intramolecular interactions between the OH-group and the  $\pi$ -electrons in the CC multiple bonds.[3]

[1] D. L. Howard and H. G. Kjaergaard, *Phys. Chem. Chem. Phys.* **10**, 4113-4118 (2008).

[2] A. L. Garden, L. Halonen, H. G. Kjaergaard, *J. Phys. Chem. A.* **112**, 7439-7447 (2008).

[3] B. J. Miller, J. R. Lane, H. G. Kjaergaard, *Phys. Chem. Chem. Phys.*, **11**, 14183-14193 (2011).

### I03: QUANTUM CHEMICAL STUDIES AND VIBRATIONAL FTIR SPECTROSCOPY OF "BLUE" SHIFTING AND "RED" SHIFTING HYDROGEN BONDS

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Vibrational spectroscopy is a powerful tool to investigate H-bonds, since shifts, intensity and band width changes give information on the local environment of the vibrating group. Most H-bonds show an elongation of the X-H covalent bond and a shift of its stretching vibration to lower wavenumbers ("red-shift"). Recent research also focuses on more unusual H-bonds with X-H bond contraction and a shift towards higher wavenumbers ("blue shift"). In addition, high level quantum-chemical calculations are indispensable to analyse experiments.

We present recent results on *ab initio* calculations and FTIR spectroscopy of H-bonded complexes containing CHCl<sub>3</sub> or HCOOH; since these molecules form both "red" and "blue" shifting H-bonds, depending on the interaction partner, they present ideal test cases to investigate the different behaviour and nature of H-bonds [1-3].

[1] S. Chung and M. Hippler, *J. Chem. Phys.* **2006**, *124*, 214316.

[2] M. Hippler, S. Hesse, and M.A. Suhm, *Phys. Chem. Chem. Phys.* **2010**, *12*, 13555.

[3] C. Mohr, C.L. Spencer, and M. Hippler, to be published.

## 104: DENSITY FUNCTIONAL THEORY FOR NON-COVALENT INTERACTIONS

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Non-covalent interactions (NCI) play an important role in many areas of science and their theoretical understanding and quantification is a main research topic in quantum chemistry. The talk addresses in particular the description of the omnipresent long- (London) and medium-range dispersion (correlation) effects in the framework of DFT<sup>[1]</sup>. In recent years it became clear that they not only have to be considered for typical van der Waals systems but also influence weak as well as strong hydrogen bonds but also "normal" thermochemistry. First, an overview about the current status of DFT for NCI and the account of dispersion effects is given. The importance of solid benchmarking on accurate, preferably CCSD(T) reference data is highlighted. General methodological recommendations regarding the use of quantum chemical methods for NCI are given. Various applications of dispersion corrected DFT in our most recent first-principles version (DFT-D3<sup>[2]</sup> using Becke-Johnson damping<sup>[3,4]</sup>) are presented. Small systems with weak hydrogen bonds as well as large protein-ligand complexes are discussed in which these interactions may sum up to 50-100 kcal/mol.

[1] S. Grimme, *WIREs Comput. Mol. Sci.* (2011), 1, 211.

[2] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.* (2010), 132, 154104.

[3] A. D. Becke and E. R. Johnson, *J. Chem. Phys.* **2005**, 122, 154101.

[4] S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.* **2011**, 32, 1456.

## 105: NONCOVALENT ORGANOCATALYSIS BASED ON HYDROGEN BONDING

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The design of “noncovalent” organocatalysts, acting solely by hydrogen bonding, is a new and emerging branch of (biomimetic) organocatalysis [1]. The lecture will present examples of catalysis effected by hydrogen bonding networks: epoxidation of olefins and Baeyer-Villiger oxidation of ketones with hydrogen peroxide in fluorinated alcohol solvents [2], kinetic and dynamic-kinetic resolution of azlactones and oxazinones, affording enantiomerically pure alpha- and beta-amino acids [3]. The transformations mentioned are of preparative value, and their scope and mechanisms will be discussed.

[1] K. Etzenbach-Effers, A. Berkessel, *Topics Curr. Chem.* **2010**, *291*, 1-27.

[2] A. Berkessel, J. A. Adrio, *J. Am. Chem. Soc.* **2006**, *128*, 13412-13420.

[3] A. Berkessel, I. Jurkiewicz, R. Mohan, *ChemCatChem* **2011**, *3*, 319-330.

## **I06: HYDROGEN BONDS AND EXCITED STATES: AN INTEGRATED QUANTUM MECHANICAL AND CLASSICAL APPROACH**

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Nowadays environmentally sensitive fluorescent dyes are largely used to monitor proteins and DNA interactions and to probe biophysical properties of membranes. However, their quantitative use is sometimes limited or even prevented by a not clear relation between the spectroscopic signal and the characteristics of the environment. This is particularly true when specific interactions between the dye and the environment are possible such as in the case of H-bonding systems. It thus becomes of utmost importance to develop accurate models that account for both the photophysical process and the environment effects in a coupled way. Due to the electronic nature of the process, a quantum-mechanical description of the dye is here compulsory while many different strategies are possible for the environment. In this talk, it will be shown that classical descriptions remain valid but only when specific requirements imposed by the process under investigation are satisfied.

## **I07: THE INFLUENCE OF HYDROGEN BONDING ON THE STRUCTURE AND PROPERTIES OF IONIC LIQUIDS**

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Potential applications of ionic liquids depend on the properties of this class of liquid material. To a large extent the structure and properties of these Coulomb systems are determined by the intermolecular interactions between anions and cations. In particular the subtle balance between Coulomb forces, hydrogen bonds and dispersion forces is of great importance for the understanding of ionic liquids.

The purpose of the present paper is to answer three questions: Do hydrogen bonds exist in these Coulomb fluids? To what extent do hydrogen bonds contribute to the overall interaction between anions and cations? And finally, are hydrogen bonds important for the structure and properties of ionic liquids? All these questions are addressed by using a suitable combination of experimental and theoretical methods. This palette includes Raman, IR, THz spectroscopy, single crystal diffraction, DFT calculations and molecular dynamics (MD) simulations.

Examples will be given for aprotic (imidazolium-based) as well as protic (ammonium-based) ionic liquids. The key statement is that although ionic liquids consist solely of anions and cations and Coulomb forces are the dominating interaction, also local interaction such as hydrogen bonding has significant influence on the structure and properties of ionic liquids. This is demonstrated for the case of melting points and viscosities. As a consequence, a variety of important properties can be tuned towards increasing working temperature, finally expanding the range of potential applications.

**I08: HYDROGEN-BONDS IN ISOLATED CLUSTERS-  
FROM PEPTIDES TO PROTON WIRES AND METAL  
CONTAINING AGGREGATES**

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Hydrogen-bonds of medium strength range among several biological and catalytically active systems. This talk focuses on the formation of hydrogen-bonds in peptides as well as on photoreactive systems based on flavonoids. In order to figure out the influence of an individual H-bond on the structure and to learn more about the driving forces to form secondary structures in peptides, isolated peptide aggregates and the process of microsolvation are analyzed by mass- and isomer-selective combined IR/UV techniques in combination with DFT calculations.

In order to investigate reaction coordinates of electronically excited states in biological relevant molecules, IR/UV investigations on hydrated flavonoids are presented including the presentation of a new IR/UV/IR/UV quadruple-resonance-spectroscopy. Further the first application of a structure sensitive IR method to a proton wire in the electronically excited state of an isolated cluster is presented.

**I09: CONTRIBUTION OF THE  $\pi$  ELECTRONS TO HYDROGEN BONDS: IR CAVITY RINGDOWN SPECTROSCOPY OF JET-COOLED MOLECULAR CLUSTERS**

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The contribution of the  $\pi$  electrons to the H-bonds has been recently attractive interests to investigate weak and moderate intermolecular interactions in biomolecules. To understand such a H-bond in a microscopic view, we observe the NH stretches of pyrrole containing clusters by IR cavity ringdown spectroscopy. In this conference, we talk about two topics. First, we show the IR spectra of 2,5-dimethylpyrrole self-aggregate and its binary clusters with pyrrole. Especially, we focus the donor-acceptor preference and methyl substitution effect in the NH- $\pi$  H-bonds of the self-aggregate trimer and the binary dimer. Second, we discuss the NH-O=C H-bond formation in pyrrole-acetone solvated clusters. Both the 1:1 and 1:2 clusters have a single H-bond between NH and C=O, while the NH stretch of the latter is red-shifted by 53 cm<sup>-1</sup> from that of the former. The NBO analysis revealed that the red-shift in the 1:2 is caused by the contribution of the  $\pi$  bonding electron on C=O group to H-bond.

[1] Y. Matsumoto and K. Honma, *J. Chem. Phys.* **127**, 184310 (2007).

[2] Y. Matsumoto and K. Honma, *Phys. Chem. Chem. Phys.* **13**, 13962 (2011).

## 110: INSIGHTS ON MATRIX ISOLATED CARBOXYLIC ACID DIMERS BY RAMAN SPECTROSCOPY

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The dimers of small carboxylic acids are of considerable interest, for example, in atmospheric chemistry and in biological context. They have attracted reasonable attention of both experimentalists and theoreticians alike as prototypes of centrosymmetric systems involving two equivalent hydrogen bonds nicely manifesting structural directionality and cooperativity.

Raman spectroscopy combined with low-temperature matrix isolation technique manifests as an efficient and sensitive approach to study molecules and their hydrogen-bonded interactions. Here, formic and acetic acid dimers isolated in argon matrices are studied, and full assignment of vibrational transitions of various hydrogen-bonded isomers is made. Special attention is paid to the intermolecular motions and their sensitivity to the mesoscopic environment. It is also demonstrated that besides using Raman measurements as a probe of the molecular motion in the studied systems, it can be used concomitantly to induce isomerization reactions and track in situ photochemical reactions. This experimental approach is easily adapted for other and more complex hydrogen-bonded systems. [1-3]

[1] A. Olbert-Majkut, J. Ahokas, J. Lundell, M. Pettersson, *Chem. Phys. Lett.* **2009**, *468*, 176-183.

[2] A. Olbert-Majkut, J. Ahokas, J. Lundell, M. Pettersson, *Phys. Chem. Chem. Phys.* **2010**, *12*, 7138-7147.

[3] A. Olbert-Majkut, J. Ahokas, J. Lundell, M. Pettersson, *J. Raman Spectrosc.* **2011**, DOI 10.1002/jrs.2909.

## 111: INFRARED SPECTROSCOPY OF SIZE-SELECTED LARGE WATER CLUSTERS

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Infrared spectroscopy is applied to size-selected neutral and protonated water clusters ( $(\text{H}_2\text{O})_n$  and  $\text{H}^+(\text{H}_2\text{O})_n$ ) in the size range of  $n=20-50$  and  $20-200$ , respectively. The free OH stretch band of the neutral water clusters shows a gradual low-frequency shift with increasing the cluster size, and the shift is interpreted in terms of the reduction of the strain in the hydrogen bond network of the water clusters [1]. In addition, hydrogen-bonded OH stretch bands of four-coordinated water sites are identified [2]. The free OH stretch band of the protonated water clusters shows that the surface of the large-sized water ( $n=100-200$ ) is covered by amorphous hydrogen bond networks. The hydrogen-bonded OH stretch band suggests the crystallization of the interior of the clusters begins at the size of  $n\sim 100$  [3].

[1] K. Mizuse, T. Hamashima, A. Fujii. *J. Phys. Chem. A*, **113**, 12134 (2009).

[2] T. Hamashima, K. Mizuse, A. Fujii, *J. Phys. Chem. A*, **115**, 620 (2011).

[3] K. Mizuse, N. Mikami, A. Fujii, *Angew. Chem. Int. Ed.*, **49**, 10119 (2010).

## **I12: DEFINING THE HYDROGEN BOND THROUGH IUPAC**

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The term 'Hydrogen Bond' has been used in the literature for nearly a century now. While its importance has been realized by physicists, chemists, biologists and material scientists, there has been a continual debate about what this term means. This debate has intensified following some important experimental results, especially in the last decade, which questioned the basis of the traditional view on hydrogen bonding. Considering the recent experimental and theoretical advances, a task group formed by IUPAC has proposed a new definition of the hydrogen bond, which emphasizes the need for evidence. [1] This talk will present the rationale behind this definition.

[1] I. E. Arunan, G. R. Desiraju, R. A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, P. Hobza, H. G. Kjaergaard, A. C. Legon, B. Mennucci and D. J. Nesbitt, *Pure Appl. Chem.* **83**, 1619 (2011).

This presentation will be followed by a panel discussion between members of the task group and conference participants

### I13: SPECTROSCOPIC STUDIES OF SOLVATION OF CHIRAL MOLECULES: FROM THE GAS PHASE TO SOLUTION

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Hydrogen (H)-bonding interactions between chiral molecules and water molecules play an essential role in life sciences since nearly all important biomolecules are chiral and most biological events take place in an aqueous environment. The structural aspects of water surrounding a chiral molecule and the fundamental roles of water in many biological processes remain subjects of intense debate. Using VCD spectroscopy, we observed that some vibrational bands of an achiral molecule, such as water, can show significant VCD strength through H-bonding to a chiral molecule.[1,2] These chirality transfer VCD features can provide detailed insight into the specific H-bonding configurations taken on by the surrounding water molecules in an aqueous solution. Using high resolution spectroscopy, in particular the newly developed broadband chirped-pulsed FTMW and the quantum cascade laser based infrared techniques, we followed the stepwise solvation of a chiral molecule. [3] The two-pronged approach described above, complemented with the *ab initio* and molecular dynamics calculations, allows one to understand such a solvation process in unprecedented details.

[1] M. Losada, H. Tran, and Y. Xu, *J. Chem. Phys.*, **2008**, *128*, 014508/1-11.

[2] G. Yang and Y. Xu, in *Top. Curr. Chem., Volume: Electronic and Magnetic Properties of Chiral Molecules and Supramolecular Architectures*, Eds R. Naaman, D. N. Beratan, D. H. Waldeck, Springer-Verlag Berlin Heidelberg, **2011**, *298*, 189-236.

[3] Z. Su and Y. Xu, *Angew. Chem.*, **2007**, *119*, 6275 – 6278; *Angew. Chem. Int. Ed.*, **2007**, *46*, 6163-6166. (VIP).

## **I14: ULTRAFAST DYNAMICS FOLLOWING PHOTOIONIZATION IN WATER: ELECTRONS, CATIONIC HOLES, AND DNA DAMAGE**

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Interaction of water with ionizing radiation is, in addition to direct DNA damage, causing radiation damage in living organisms and it is also important for nuclear waste treatment. Upon photoionization in water an electron and a cationic hole are formed, therefore, we follow the fate of both. To the former, we present a computational study of the structure and dynamics of an excess electron in a medium-sized water cluster aimed at addressing the question of interior vs. exterior solvation, electron localization and its quenching with a hydrated proton leading to the formation of a hydrogen atom. To the later, we calculate the ultrafast relaxation of a cationic hole in water dimer and in the aqueous bulk followed by formation of an OH radical. Ab initio Born-Oppenheimer molecular dynamics simulations are performed with the exchange-correlation functionals corrected for self-interaction error and augmented by an empirical dispersion term.

**I15: BIOMOLECULAR FLEXIBILITY AND SOLVATION:  
HOW A SINGLE WATER MOLECULE FOLDS A  
MODEL PEPTIDE CHAIN**

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Hydration of a model peptide chain, N-acetyl-phenylalanine-amide (NAPA), has been investigated by infrared-ultraviolet (IR/UV) double resonance spectroscopy[1]. The IR spectra of 4 conformations of the 1:1 water:peptide complexes have been recorded with a resolution of  $\sim 1 \text{ cm}^{-1}$  in the OH and NH stretch domain, and have been assigned by comparison with scaled harmonic frequency calculations of conformations optimized at the RI-B97-D/TZVPP level. The structural arrangements of the solvated peptide are revealed, as well as the preferred solvation sites occupied by the water molecule. The out-of-equilibrium distribution observed can finally be explained by different kinds of hydration occurring on the isolated peptides: (a) solvation on a rigid site with no significant structural change of the peptide, (b) solvation on flexible site inducing deformations of the backbone and (c) solvation which triggers backbone isomerizations as the folding  $\beta$ -strand into  $\gamma$ -turn structures.

[1] H. S. Biswal, Y. Loquais, B. Tardivel, E. Gloaguen, J. M. Mons, *J. Am. Chem. Soc.* **2011**, *133*, 3931.

**I16: HARNESSING THE EXCITED-STATE  
INTRAMOLECULAR PROTON TRANSFER  
REACTION; NEW ASPECT AND APPLICATIONS**

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In this talk I will first provide a general aspect regarding excited-state intramolecular proton transfer (ESIPT). Depending on the hydrogen bonding strength, ESIPT molecules are classified into strong- and weak- coupling cases, for which the associated hydrogen bonding strength and hence the proton-transfer dynamics are well differentiated. In another approach, novel ESIPT molecules are ingeniously designed, so that the proton transfer is associated with significant changes of dipole moment due to its coupling with charge transfer effect. In this case, it is of interest as well as importance to investigate the role of solvent polarity/relaxation channeling into the ESIPT dynamics/thermodynamics. Several prototypical examples will be discussed. Finally, via tuning the thermodynamics of the ESIPT reaction, I like to present as well as to prove a concept in that the white light generation can be achieved intrinsically in a single ESIPT system, suited for organic light emitting diodes.

[1] K.-Y. Chen, Y.-M. Cheng, C.-H. Lai, C.-C. Hsu, M.-L. Ho, G.-H. Lee, P.-T. Chou, *J. Am. Chem. Soc.* **2007**, *129*, 534.

[2] C.-C. Hsieh, C.-M. Jiang, P.-T. Chou, *Acc. Chem. Res.* **2010**, *43*, 1364.

[3] C.-C. Hsieh, P.-T. Chou, C.-W. Shih, W.-T. Chuang, M.-W. Chung, J. Lee and T. J. Joo, *Am. Chem. Soc.* **2011**, *133*, 2932.

## **I17: FIRST PRINCIPLES ANHARMONIC VIBRATIONAL THEORY FOR HYDROGEN-BONDED CLUSTERS**

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An extremely broad band in the range of  $3000\text{ cm}^{-1}$  is the well-known signature of hydrogen bonds. It is so unique that one can easily tell the existence of hydrogen bond with a single look at the vibrational spectrum. However, very little is known on the mechanism of the broadening. What makes the band distinguished, and what is the underlying physics? Here, we have developed theoretical methods to answer these questions. The crux of the problem is an exponential increase in the cost for (1) evaluating anharmonic force constants and (2) solving the vibrational Schrodinger equation. The former exploits a multiresolution technique [1,2] on top of ab initio electronic structure theories. An efficient solver, vibrational quasi-degenerate perturbation theory [3], is proposed, which describes the strong resonance and the remaining weak, vast number of interactions in a balanced fashion. The method is applied to a series of biomolecules: nucleic acid base pairs, etc.

[1] P. Seidler, T. Kaga, K. Yagi, O. Christiansen, and K. Hirao, *CPL*, **483**, 138 (2009).

[2] K. Yagi, S. Hirata, and K. Hirao, *TCA*, **118**, 681 (2007).

[3] K. Yagi, S. Hirata, and K. Hirao, *PCCP*, **10**, 1781 (2008).

## I18: HIGH-TEMPERATURE FERROELECTRICITY IN HYDROGEN-BONDED ORGANIC CRYSTALS

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Ferroelectricity is the property of nonvolatile electric polarization that can be reversed by the application of an external electric field. Ferroelectric materials have been used in memory, capacitors, piezoelectric devices, and optical devices. Here we show direct observation of the electric polarization - field hysteresis on the molecular crystals with beta-diketone enol  $O=C-C=C-OH$  or carboxylic unit; croconic acid ( $C_5H_2O_5$ ) [1], cyclobutene-1,2-dicarboxylic acid, 2-phenylmalondialdehyde, and so on [2]. The bistability of the hydrogen-bonding chains has been proved to functionalize the ferroelectricity of high polarization performance at room temperature. The mechanism is rather irrespective of the details of local bonding configurations, and then this design principle is not limited to the specific molecules as demonstrated here but could be adaptive to diverse class of materials even including polymeric and biomolecular systems.

[1] S. Horiuchi, Y. Tokunaga, G. Giovannetti, S. Picozzi, H. Itoh, R. Shimano, R. Kumai, Y. Tokura, *Nature* **2010**, *463*, 789.

[2] S. Horiuchi, R. Kumai, Y. Tokura, *Adv. Mater.* **2011**, *23*, 2098.

## **I19: HIGH-PRESSURE CRYSTALLISATION OF HYDROGEN-BONDED MOLECULAR COMPOUNDS: TOWARDS AN UNDERSTANDING OF SOLID-STATE POLYMORPHISM**

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The importance of polymorphism, solvate and hydrate formation in the crystallisation of organic compounds is widely recognised within the industrial and academic communities; physical form discovery and control are currently the subject of intense research activity.[1] Recent studies have demonstrated that high pressure is a powerful means for inducing phase transitions in molecular compounds; *in situ* high-pressure crystallisation from solution has proven particularly effective for generating new physical forms of pharmaceuticals.[2]

Through a series of case studies on hydrogen-bonded molecular crystals obtained by *in situ* crystallisation, it will be shown how at high pressure certain combinations of hydrogen bonds can be stabilised that are otherwise not found at ambient pressure. This knowledge provides further qualitative and quantitative information towards a better understanding of intermolecular interactions, crystal packing and ultimately solid-state polymorphism.

[1] J. Bernstein, *Cryst. Growth & Des.* **2011**, *11*(3), 632-650.

[2] F. P. A. Fabbiani in: "High-Pressure Crystallography: From fundamental Phenomena to Technological Applications", Eds. E. Boldyreva and P. Dera, *NATO Science for Peace and Security Series: B – Physics and Biophysics*, Springer, **2010**, 545-558.

## **I20: DYNAMICS OF WATER NEXT TO PROTEINS**

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The biological function of proteins is very sensitive to their hydration layer dynamics. Despite an active study over the last decades, several key questions remain, including e.g. the magnitude of the protein-induced slowdown on water dynamics (from a twofold retardation to a near immobilization), the respective roles played by the protein topology and chemistry, and the presence of collective behaviors within the protein hydration layer. Based on simulations and the extended jump model we recently developed, we have investigated the water dynamics around lysozyme.

We show that the large majority of waters within the hydration layer are moderately slowed down with respect to the bulk (factor < 2) due to a topological effect, while a minority of waters are more retarded due to buried protein sites which are strong hydrogen-bond acceptors.

Our model provides the first molecular-scale picture of protein hydration dynamics, and these results are in excellent agreement with recent NMR data.